

CHELATE-STABILIZED ALKYLIDENE COMPLEXES
OF MOLYBDENUM AND TUNGSTEN

By

WILLIAM M. VAUGHAN

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1995

ACKNOWLEDGMENTS

Enter to think God's thoughts after Him. Go forth to apply His thoughts in service.

Townes Randolph Leigh

That statement on the facade of Leigh Hall, along with the names of great scientists and their gargoyles, has done much to inspire and humble over the past few years. The chemists of Leigh's time would be amazed at the strides that have been made, but they would have expected no less. I could only hope that I too have made a small contribution to the quality reputation of the Department of Chemistry at the University of Florida.

I have great appreciation for the guidance and support of my research director, Dr. James M. Boncella. From Jim, I have not only begun to learn the art of science, but to understand the true excitement in learning and discovery.

I thank the members of my committee, Professors David Richardson, Bill Jones, Ken Wagener and Guerry McClellan, for their time, advice and encouragement. Discussions with Profs. Richardson and Jones were instrumental in developing the mechanisms in Chapter Three. A special thanks is extended to Prof. Wagener. I often pass along "the best advice I ever got about graduate school" to anyone that will listen.

The research of this dissertation is greatly dependent on the assistance and many helpful conversations with Drs. Khalil Abboud, Roy King and David Powell. Maria Ospina with Dr. Powell collected the CIMS data in Chapter Three.

One can learn so much from the people around them, and my fellow group members over the years have made that all too evident. Those people that have made research so enjoyable are Gaines Martin, Laura Bloesch, Scott Gamble, Larry Villanueva, Percy Doufou, Jerrold Miller, Wang Shu-Yu, Jon Penney and Faisal Shafiq. Justine Roth

has been an inspiration over the last year by the consuming interest she takes with research. Dan VanderLende has been a perennial source of motivation and friendship.

Dennis W. Smith, Jr. has been a constant best friend throughout graduate school, and anyone who knows him will know why. With whom else one would attempt to conquer the continent of Europe in a fortnight, and truly believe that one would? Kathy Novak will always remain a special friend, and it is ironic that in thinking of someone who is so eloquent with words, I cannot think of how to describe how she has benefited my experience at Florida.

My parents, Michael and Kay, and my brother Steven define encouragement and support more than anyone. Through Sunday evening phone conversations, the demands of research never seemed quite so bad.

I finally thank my fiancée, Pamela Pippin. One day it was extremely obvious why and for whom I work so hard, and Pam's understanding and commitment have been unfaltering during the writing of this dissertation.

TABLE OF CONTENTS

ACKNOWLEDGMENTS.....	ii
ABSTRACT	vi
CHAPTERS	
1 INTRODUCTION AND BACKGROUND.....	1
Transition Metal-Ligand Multiple Bonds	2
Transition Metal Alkylidene Complexes.....	5
The Nature of Metal-Carbon Double Bonds.....	5
Synthesis and Characterization of Metal Alkylidenes.....	10
Reactivity of Metal Alkylidene Ligands	14
Olefin Metathesis	16
Chelated Transition Metal Alkylidene Complexes.....	21
2 MOLYBDENUM IMIDO ALKYLIDENE COMPLEXES STABILIZED BY HYDRIDOTRIS(PYRAZOLYL)BORATE	26
Neutral Molybdenum Imido Alkylidene Complexes	27
Synthesis of $\text{TpMo}(\text{CHC}(\text{Me})_2\text{Ph})(\text{NAr})(\text{OTf})$	27
Crystal Structure of $\text{TpMo}(\text{CHC}(\text{Me})_2\text{Ph})(\text{NAr})(\text{OTf})$	29
Synthesis of $\text{TpMo}(\text{CH}_2\text{C}(\text{Me})_2\text{Ph})(\text{NAr})(\text{O})$	32
Crystal Structure of $\text{TpMo}(\text{CH}_2\text{C}(\text{Me})_2\text{Ph})(\text{NAr})(\text{O})$	33
Crystal Structure of $[\text{TpMo}(\text{NAr})(\text{O})]_2\text{O}$	37
Synthesis of $\text{TpMo}(\text{CHC}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{OCH}_3)$	39
Synthesis of $\text{TpMo}(\text{CC}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{OCH}_3)$	40
Crystal Structure Determination of $\text{TpMo}(\text{CHC}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{OCH}_3)$ and $\text{TpMo}(\text{CC}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{OCH}_3)$	45
Cationic Molybdenum Imido Alkylidene Complexes	49
Synthesis of $\text{TpMo}(\text{CHC}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{CH}_3)$	50
Synthetic Routes to Cationic Molybdenum Imido Alkylidene Complexes	51
The <i>Trans</i> Influence of Ligands in Tp Molybdenum Complexes.....	57
Rotational Isomerism of the Molybdenum-Alkylidene Bond	58
Polymerization Studies	62
Conclusion	64
3 THE KINETICS AND MECHANISMS OF REACTIONS INVOLVING PHENYLENEDIAMIDO TUNGSTEN COMPLEXES.....	65
Synthesis, Characterization and Structure of the Metallacycle Complex.....	67
Kinetics of the Formation of the Metallacycle Complex	72

Kinetics of the Formation of the Alkylidene Complex...	76
A Closer Look at the Role of Phosphine	77
Interconversion of the Metallacycle and the Alkylidene Complexes.....	81
Deuterium-Labeling Studies.....	83
Chemical Ionization Mass Spectrometry Study	84
Deuterium NMR Spectroscopy.....	87
Kinetic Isotope Effects in the Formation of the Metallacycle and the Alkylidene Complexes	89
Proposed Mechanistic Scheme.....	91
Conclusion	93
 4 EXPERIMENTAL PROCEDURES	94
Materials and Methods.....	94
Syntheses.....	95
TpMo(CHC(Me) ₂ Ph)(NAr)(OTf) (1).....	95
TpMo(CH ₂ C(Me) ₂ Ph)(NAr)(O) (2)	95
TpMo(CHC(CH ₃) ₂ Ph)(NAr)(OCH ₃) (4)	96
TpMo(CC(CH ₃) ₂ Ph)(NAr)(OCH ₃) (5)	97
TpMo(CHC(CH ₃) ₂ Ph)(NAr)(CH ₃) (6)	98
[TpMo(CHC(CH ₃) ₂ Ph)(NAr)(Et ₂ O)][BAR' ₄] (7).....	99
[TpMo(CHC(CH ₃) ₂ Ph)(NAr)(NCCH ₃)] [B(C ₆ F ₅) ₄] (8).....	100
[TpMo(CHC(CH ₃) ₂ Ph)(NAr)(NCCH ₃)] [B(CH ₃)(C ₆ F ₅) ₃] (9)	100
[TpMo(CHC(CH ₃) ₂ Ph)(NAr)(THF)] [B(CH ₃)(C ₆ F ₅) ₃] (10)	101
[TpMo(CHC(CH ₃) ₂ Ph)(NAr)(P(CH ₃) ₃)] [OSO ₂ CF ₃] (11).....	102
[(H ₃ CO) ₂ C ₆ H ₂ (NSi(CH ₃) ₃) ₂]W(NPh)(Cl) ₂ (17)	103
[(H ₃ CO) ₂ C ₆ H ₂ (NSi(CH ₃) ₃) ₂]W(NPh)(Cl) ₂ (P(CH ₃) ₃) (19).....	104
Crystallographic Studies.....	104
X-ray data collection and structure refinement for compounds 2 and 3.....	104
X-ray data collection and structure refinement for compounds 4 and 5.....	106
X-ray data collection and structure refinement for compounds 16	107
Alkylidene Rotational Studies.....	108
Polymerizations.....	109
ROMP reactions by 1 and 6 with AlCl ₃	109
Oligomerization of 1,9-decadiene by 1 and 6 with AlCl ₃	110
Thermolysis Kinetics	110
UV-VIS Spectroscopy Studies	111
Mass Spectrometry of Neopentane- <i>d</i> _n	112
Deuterium NMR Spectroscopy	112
 APPENDICES.....	113
A TABLES OF CRYSTALLOGRAPHIC DATA.....	114
B TABLES OF KINETIC AND CIMS DATA.....	171
 LIST OF REFERENCES	176
 BIOGRAPHICAL SKETCH.....	183

Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

CHELATE-STABILIZED ALKYLIDENE COMPLEXES
OF MOLYBDENUM AND TUNGSTEN

By

William M. Vaughan

May, 1995

Chairman: James M. Boncella
Major Department: Chemistry

Two chelating ligands, hydridotris(pyrazolyl)borate (Tp) and N,N'-bis(trimethylsilyl)phenylenediamide (TMS₂pda), were used to stabilize imido alkylidene complexes of molybdenum and tungsten. The tridentate Tp ligand successfully stabilized a number of molybdenum complexes of the formula TpMo(ChC(CH₃)₂Ph)(N(2,6-*i*Pr₂C₆H₃)(X) where X is triflate, methoxy or methyl substituents. The stability imparted by the ligand system allowed for numerous synthetic transformations not commonly observed for high oxidation state metal alkylidene complexes. These include the isolation of hydrolysis products, base-catalyzed proton transfer from an alkylidene ligand to an imido ligand, and the preparation of cationic molybdenum alkylidenes by several methods. Differing rates of rotation of the molybdenum-alkylidene double bond are correlated to the electronic properties of the X substituent. Polymerization studies indicate that the coordinatively saturated complexes are inactive as olefin metathesis catalysts, but by addition of a Lewis acid cocatalyst, ring-opening metathesis polymerizations are catalyzed.

The reactions of tungsten imido complexes stabilized by TMS₂pda ligand have been studied. Thermolysis of complex (TMS₂pda)W(NPh)(CH₂C(CH₃)₃)₂ (**13**) gives a metallasilylcycle complex [(Me₃SiN)C₆H₄(N'SiMe₂CH₂)]W(NPh)(CH₂C(CH₃)₃) (**16**), and in the presence of trimethylphosphine, the alkylidene complex (TMS₂pda)W(NPh)(CHC(CH₃)₃)(P(CH₃)₃) (**14**), is isolated. Complexes **16** and **14** can be interconverted by the addition or abstraction of PMe₃. The mechanisms of these transformations were studied by ¹H NMR kinetics and deuterium-labeling studies. A mechanistic scheme is proposed based on the observations that two competing abstraction pathways are present and that PMe₃ is not involved in the rate determining step.

CHAPTER 1 BACKGROUND AND INTRODUCTION

Our interest in the synthesis of novel transition metal alkylidene complexes is linked to the birth of coordination polymerizations in the early 1950s.¹ The chemistry world was inundated by a flurry of research centered upon the discoveries of Ziegler and Natta that transition metal halides and aluminum alkyls polymerize ethylene and propylene to give high molecular weight polyethylene and stereoregular polypropylene under mild conditions. Naturally, their Nobel Prize-winning discovery prompted research extending this new concept to all metals in the periodic table. However, when molybdenum and tungsten were employed, researchers stumbled upon olefin metathesis and the ring-opening polymerization of cyclic olefins.

The nature of these early, heterogeneous catalysts made the characterization of the catalytic active species extremely difficult, but this "blissful ignorance" did not hinder the application of this new reaction to numerous industrial processes.² More than 10 years after the first reports of olefin metathesis, Hérrison and Chauvin proposed that metal-carbon double bonds were the reactive moiety as a result of detailed kinetic and mechanistic studies by numerous researchers.³ Eventually, the preparation of isolable transition metal alkylidene complexes that catalyzed olefin metathesis solidified support for the Chauvin mechanism, and these well-defined alkylidene complexes were more amenable to systematic variations of the metal and ligand environment.² As a result, the in-depth spectroscopic, kinetic and mechanistic study of discrete molecules have led to catalytic systems that are more active, more efficient, and more selective. The goals of achieving better catalysts are the incentive for the research described herein with the directive of

synthesizing and characterizing novel high oxidation state transition metal complexes for their application to olefin metathesis.

Transition Metal-Ligand Multiple Bonds

Highly electrophilic d^0 metal centers are capable of forming multiple bonds with carbon, nitrogen, and oxygen by a σ bond and one or two π bonds between the metal $d\pi$ and ligand $p\pi$ orbitals.^{4,5} The formal oxidation state of the ligands is that of their closed-shell anions, thus the triply-bonded nitrido^{6,7} and alkylidyne ligands are N^{3-} and CR^{3-} , and the doubly-bonded oxo, imido, and alkylidene ligands are O^{2-} , NR^{2-} , and CR^{2-} , respectively. This formalized bonding description of a d^0 metal center and anionic ligands reflects the observed electrophilicity of the metal center and the nucleophilicity of the ligand atoms.

The bonding orbitals involved in forming the metal-ligand multiple bonds are similar for the above ligands since oxo, imido, nitrido, and alkylidyne ligands are isoelectronic, involving empty metal $d\pi$ orbitals and filled ligand $p\pi$ orbitals. As indicated in Figure 1.1, if the metal-ligand bond is taken to lie along the z axis of an xyz coordinate

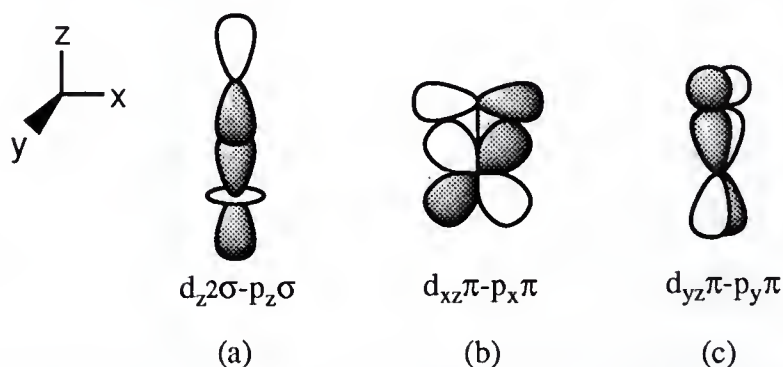


Figure 1.1. Metal-ligand bonding orbitals. a) The $d\sigma-p\sigma$ bond; b) A $d\pi-p\pi$ bond in xz plane; c) A $d\pi-p\pi$ bond in yz plane orthogonal to (b).

system, a σ bond lies coincidental with the z axis, one π bond is formed between the empty metal d_{xz} and the filled ligand p_x orbitals, and a second π bond is possible between the

metal d_{yz} and ligand p_y orbitals. In simple valence bonding terms, the trianionic nitrido and alkylidyne⁸ ligands form three bonds, and the dianionic oxo, imido, and alkylidene ligands form double bonds.

The oxo⁹ and imido^{10,11} ligands can be viewed as isoelectronic with the nitrido and alkylidyne ligands because of their ability to donate a lone pair of electrons to an empty $d\pi$ orbital (Figure 1.2). Metal-oxo and metal-imido groups are considered to be triply bonded whenever the formal electron count at the metal center is less than eighteen. Experimental evidence for triply bonded oxo and imido ligands comes from ν_{MN} and ν_{MO} determined by infrared spectroscopy and structural data determined by x-ray crystallography.^{4,10} Higher frequency stretching energies and shorter metal-ligand distances are observed for triply bonded ligands, and in the case of imido ligands, the rehybridization of the nitrogen atom results in M-N-R bond angles approaching linearity. This additional π stabilization provided by oxo and imido ligands makes the use of such ligands highly desirable in stabilizing electropositive d^0 metal centers, and the ligands are often employed as inert "spectator" ligands in the synthesis of stable transition metal complexes.¹²

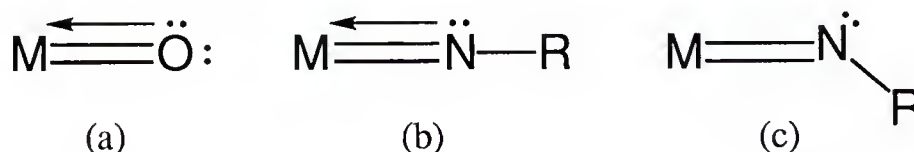


Figure 1.2. Bond orders of oxo and imido ligands. a) A oxo triple bond; b) A linear imido triple bond; c) A bent imido double bond.

With this understanding of the nature of multiple bonds between transition metals and ligands, the consequence of more than one metal-ligand multiple bond in a complex will be considered. The d^0 metal center has only three unfilled orbitals of π symmetry available for bonding. For octahedral complexes, only three $d\pi$ - $p\pi$ bonds can exist in a complex in compliance with the eighteen electron rule. In order to maximize π bonding, multiply bonded ligands are oriented *cis* to one another.¹³⁻¹⁶ A *trans* orientation could result in competition between two π bonded ligands for the same empty d orbital,

thus destabilizing the π interactions. The advantage of *cis*-oriented ligands is demonstrated in the orbital diagram shown (Figure 1.3), in which the π interactions of a triply bonded oxo ligand and a doubly bonded alkylidene ligand each involve different, mutually orthogonal $d\pi$ orbitals.

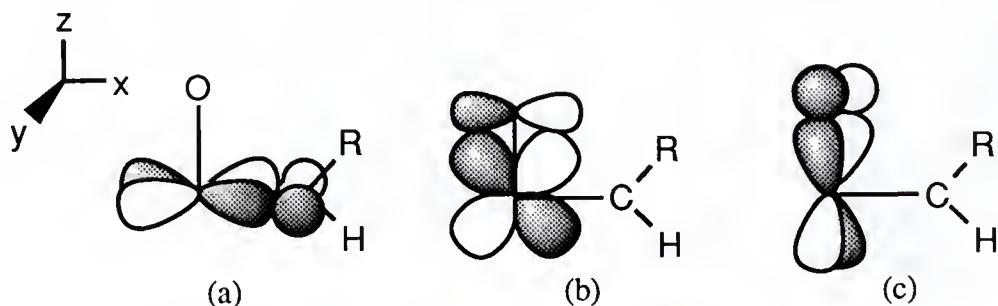


Figure 1.3. Metal-ligand interaction with two multiply bonded ligands. a) A metal-alkylidene π bond; b) A metal-oxo π bond; c) A metal-oxo π bond orthogonal to (b).

The limit of three π bonds due to orbital competition is seen in the structure of $\text{Mo}(\text{NPh})_2(\text{S}_2\text{CNEt}_2)_2$, in which the possibility of two triply bonded imido ligands is precluded (Figure 1.4). The x-ray crystal structure of $\text{Mo}(\text{NPh})_2(\text{S}_2\text{CNEt}_2)_2$ shows one of the imido ligands to be nearly linear ($169.4(4)^\circ$, triply bonded) and the other imido ligand to be bent ($139.4(4)^\circ$, doubly bonded).^{17,18}

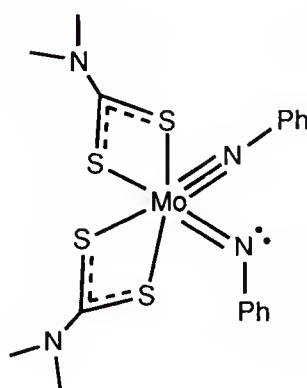


Figure 1.4. Metal-ligand multiple bond competition between two imido ligands.

The concepts presented for the orbital interactions of metal-ligand multiple bonds are useful tools in the analysis and description of these complexes, and reference to these

concepts will be used to explain observations and results concerning the metal imido alkylidene complexes throughout this dissertation.

Transition Metal Alkylidene Complexes

Metal-carbon double bonds are the focus of this research, and in this section, the nature of metal alkylidenes will be reviewed more extensively. Also, the synthesis, characterization, and reactivity of metal alkylidenes will be briefly surveyed.

The Nature of Metal-Carbon Double Bonds

Transition metal alkylidenes or carbenes are capable of forming only one π bond due to the sp^2 hybridization at the carbon atom. In classifying metal-carbon doubly bonded complexes, there is a distinction drawn between Schrock-type alkylidene and Fischer-type carbene complexes.^{4,5} The difference between these two types of ligands is determined by the oxidation state of the metal, the electronic configuration of the ligand, and the substituents on the α -carbon of the ligand.

In Fischer-type carbenes, the carbon atom is considered to be electrophilic. These complexes characteristically contain transition metals (groups 6-9) in low oxidation states and have π -donor substituents (heteroatoms, phenyl ring) on the α -carbon.¹⁹ E.O. Fischer reported the first example, $W(CO)_5(=C(CH_3)(OCH_3))$, in 1964 in which the tungsten atom is in its zero oxidation state and the carbene ligand is considered to be a neutral donor.²⁰ Shown in Figure 1.5, the carbene fragment in Fischer complexes is considered to be a singlet carbene donating its electron pair to an empty $d\sigma$ orbital.⁴ The π bond results from overlap of a filled $d\pi$ metal orbital with the empty $p\pi$ carbon orbital. For the later transition metals, the $d\pi$ orbital is lower in energy than the $p\pi$ orbital, and the bond is polarized in the M^--C^+ direction resulting in an electrophilic carbon atom.

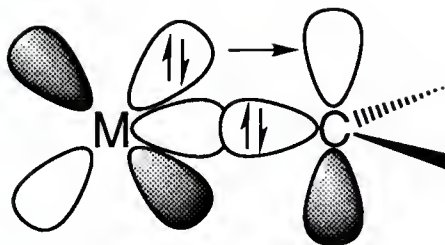


Figure 1.5. Electronic structure of a Fischer-type carbene.

The Schrock-type alkylidene, however, is considered to be nucleophilic. Alkylidene complexes contain high-valent, early transition metals, most commonly in the d^0 oxidation state. The α -carbon is substituted by hydrogen or alkyl groups, and the highly electrophilic metal center is often stabilized by π -donating ancillary ligands, such as oxo, imido, alkoxide, or halide ligands. R.R. Schrock reported the first example, $\text{Ta}(\text{CHC}(\text{CH}_3)_3)(\text{CH}_2\text{C}(\text{CH}_3)_3)_3$ in 1973.²¹ The bonding in metal alkylidenes can be viewed in different ways (Figure 1.6), and a number of theoretical investigations suggest the bond descriptions vary depending on the complex in question. An ionic valence bond description considers the alkylidene fragment as a CR_2^{2-} carbanion interacting with two empty metal d orbitals, such as was described in the previous section for oxo and imido complexes. Other descriptions suggest a more covalent bond consisting of a triplet carbene fragment interacting with a triplet metal fragment.^{22,23} Reality lies somewhere between these two extremes.

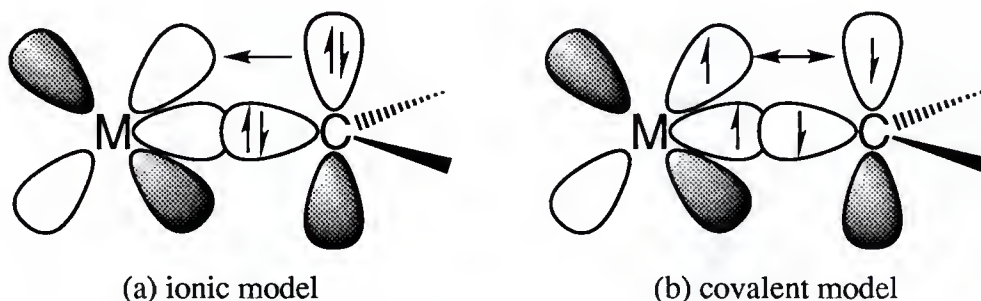


Figure 1.6. Bonding models for Schrock-type alkylidenes. a) Ionic model with CR_2^{2-} carbon fragment; b) Covalent model with 'ethylene-like' bonding.

The orbitals for early transition metals are higher in energy than the carbon orbitals resulting in the metal alkylidene bond being polarized in the M^+-C^- direction. The higher this energy difference is the more ionic the nature of the bond is, and the ionic valence description is of more importance. However, this energy difference for carbon ligands is not as great as the difference for the more electronegative oxygen or nitrogen ligands, and thus metal alkylidene bonds are increasingly covalent compared to oxo and imido bonds. Such an "ethylene-like" description is evidenced by the high barriers to rotation of metal-carbon double bonds. The mechanism of metal-carbon double bond rotation is described later in this section.

The transition metal involved in the existence of alkylidene complexes is of strict importance.⁴ Schrock-type terminal alkylidenes complexes have been reported for zirconium,²⁴ titanium,²⁵ tantalum, molybdenum, tungsten, rhenium,²⁶ ruthenium²⁷ and osmium.²⁸ However, most d^0 alkylidene complexes are found in groups 5, 6 and 7, and alkylidene complexes found outside these groups often have ambiguous oxidation states.⁸ Without a doubt, molybdenum and tungsten are the most common and successful metals in stabilizing metal-carbon double bonds. Groups 3, 4, and the late transition metals tend to form metal-carbon single bonds rather than double bonds. Examples in Figure 1.7 are the Tebbe-Grubbs reagent, $Cp_2Ti(\mu-CH_2)(\mu-Cl)Al(CH_3)_2$ in which the nucleophilic methyldiene ligand bridges the titanium and Lewis acidic aluminum atoms.²⁹ However, in the presence of phosphines, the methyldiene complex is stable.²⁵ Also, platinum,³⁰ iridium,³⁰ ruthenium,³¹ rhodium³² and thorium³³ complexes exist as metallacycles (two M-C single bonds) rather than as alkylidenes (one M-C double bond).

The reason for this periodic trend is not well understood. However, it has been suggested that the d orbitals of the early transition metals are very high in energy, resulting in extremely polar metal-carbon bonds.⁴ The increased electron density and basicity at the carbon atom causes the alkylidene ligand to bridge to Lewis acids. At the other end of the transition metal series, the d orbitals of the metals are too contracted to support $d\pi-p\pi$

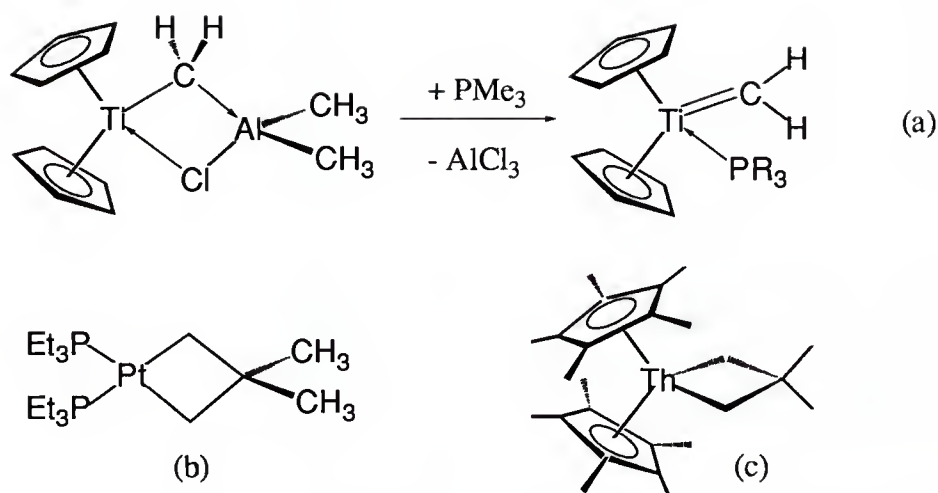


Figure 1.7. Examples of groups 3, 4, and late transition metals favoring single bonds rather than multiple bonds. a) Tebbe-Grubbs reagent; b) A platinum metallacycle; c) A thorium metallacycle.

overlap, and bridged structures are again favored.²³ Thus, the considerations of bond polarity and orbital overlap result in the preponderance of metal alkylidene complexes being found with groups 5, 6 and 7.

Schrock-type alkylidene complexes are often stabilized by oxo and imido ligands. These metal oxo/imido alkylidene complexes invariably maximize $d\pi$ - $p\pi$ bonding by adapting a mutually *cis* orientation.¹⁴ This allows each ligand $p\pi$ orbital to overlap with a separate $d\pi$ orbital. As a result, the substituents on the alkylidene ligand lie in the $\text{C}_\alpha\text{-M-Y}$ plane, where Y is O or N of the spectator ligand. For mono-substituted alkylidenes, the *syn* or *s-cis* orientation has the hydrocarbyl substituent situated towards the spectator ligand, and the *anti* or *s-trans* orientation has the substituent situated away from the spectator ligand (Figure 1.8). The *syn* and *anti* rotational isomers are referred to as rotamers in the literature.³⁴ Though the *syn* rotamer may seem to be not favored thermodynamically due to steric arguments, it is observed in most compounds to be the more stable isomer. This result is rationalized by the possibility of agostic interactions between a hydrogen substituent on the α -carbon and the metal in electronically and coordinatively unsaturated complexes.

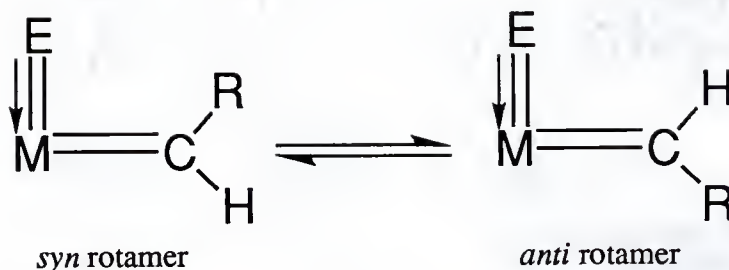


Figure 1.8. Depiction of *syn* and *anti* rotamers for oxo/imido alkylidenes. (E = O, NR)

Recently, in-depth studies have dealt with relative stabilities of the two alkylidene rotamers and the energetic barriers that separate them.³⁴⁻³⁶ The *syn* and *anti* rotamers can be interconverted either thermally or photochemically, and rotational barriers have been reported ranging from 12 to >21 kcal/mol.⁵ For transition metal imido alkylidene complexes, a mechanism for alkylidene rotation has been suggested and theoretical calculations support such a barrier (Figure 1.9).^{14,37} The mechanism suggests that the barrier to rotation is stabilized by the reforming of a metal-alkylidene π bond in the

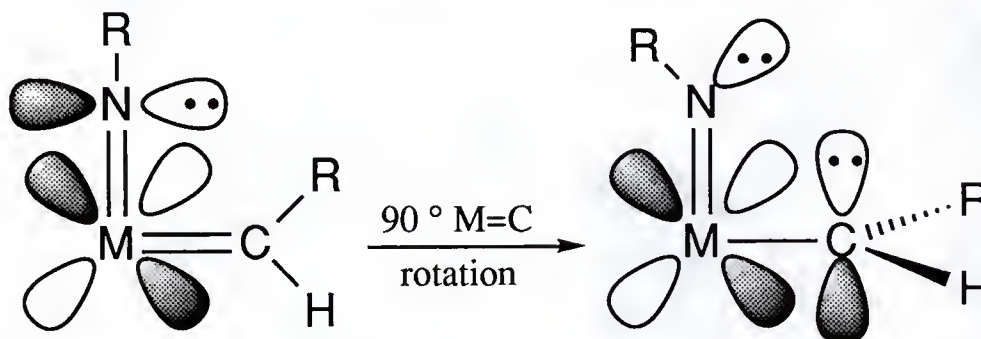


Figure 1.9. Mechanism for the rotation of a metal-carbon double bond.

transition state. In the ground state, the imido is triply bonded with an sp hybridized nitrogen atom. Upon a 90° rotation of the metal-carbon bond, the sp nitrogen can rehybridize to sp^2 , giving a lone pair on the nitrogen and a bent imido bond. This allows the filled p orbital of the alkylidene carbon to donate to the $d\pi$ orbital vacated by the nitrogen lone pair. This mechanism allows for a metal-alkylidene double bond in both the ground state and the transition state, and the more electronegative nitrogen atom

accommodates the excess electron density rather than the carbon. Alternatively, the bonding in the transition state could be described as a three-center, four electron bond, and rehybridization of the nitrogen atom would not be necessary.

Since its discovery, the metal-carbon double bond has received much study, and thus much can be said about its nature. However, considerable strides have been made to improve the synthesis and stability of metal-carbon double bonds. The following section will describe synthetic routes to metal alkylidene complexes as well as the effects of ancillary ligands on their stability.

Synthesis and Characterization of Metal Alkylidenes

The synthetic routes to transition metal alkylidenes parallel organic reactions that result in the formation of carbon-carbon double bonds. These parallels include elimination across a metal-carbon single bond, addition across a metal-carbon triple bond, and carbene transfer by phosphonium ylides, or Wittig reagents.

The most widespread example of alkylidene bond formation is abstraction of an α -proton of a metal alkyl.⁴ The first example was Schrock's compound, $\text{Ta}(\text{CHC}(\text{CH}_3)_3)(\text{CH}_2\text{C}(\text{CH}_3)_3)_3$, from the reaction of two equivalents of neopentyl lithium with $\text{Ta}(\text{CH}_2\text{C}(\text{CH}_3)_3)_3\text{Cl}_2$ (Figure 1.10).³⁸ The α -abstraction results during dehydrohalogenation of the tantalum-carbon bond promoted by a strong base, the neopentyl carbanion. Dehydrohalogenation is also seen in the deprotonation of $\text{Re}(\text{NPh})_2(\text{CH}_2\text{C}(\text{CH}_3)_3)\text{Cl}_2$ to give an alkylidene complex.³⁹

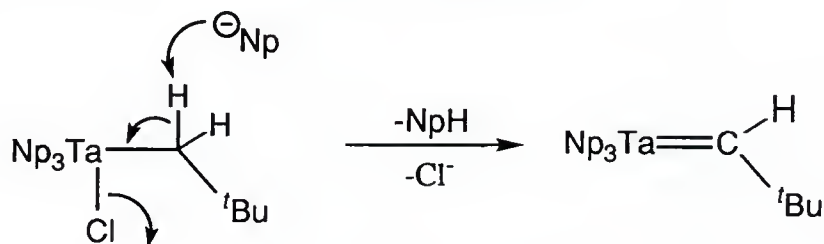


Figure 1.10. Dehydrohalogenation mechanism resulting in a tantalum alkylidene complex.

Intramolecular abstraction of α -proton by another alkyl ligand is seen in a number of systems, and this mechanism depends greatly on the steric environment of the metal center. Heating or adding a coordinating ligand promotes α -abstraction in bisalkyl complexes that do not spontaneously give alkylidene. Because of their steric bulk, the neopentyl ligand and the related neophyl ligand ($-\text{CH}_2\text{CMe}_2\text{Ph}$) have a particular synthetic advantage. In fact, most syntheses of stable, terminal alkylidene complexes employ these bulky alkyl ligands. Also, the neopentyl and neophyl ligands have no β -protons, and thus β -hydride reductive elimination pathways are precluded. Examples of intramolecular abstraction included the syntheses of $\text{M}(\text{CHC}(\text{CH}_3)_3)(\text{NAr})(\text{CH}_2\text{C}(\text{CH}_3)_3)_2$ ⁴⁰ and $\text{M}(\text{CHC}(\text{CH}_3)_3)(\text{NAr})(\text{DME})(\text{X})_2$ ^{41,42} ($\text{M} = \text{W}, \text{Mo}$; $\text{NAr} = 2,6$ -diisopropylphenylimido; $\text{DME} = \text{dimethoxyethane}$; $\text{X} = \text{Cl}, \text{OSO}_2\text{CF}_3$). In the case of $\text{M}(\text{CHC}(\text{CH}_3)_3)(\text{NAr})(\text{CH}_2\text{C}(\text{CH}_3)_3)_2$ (Figure 1.11a), the formation of the alkylidene is spontaneous with the increased steric bulk at the metal center. For $\text{M}(\text{CHC}(\text{CH}_3)_3)(\text{NAr})(\text{DME})(\text{X})_2$ (Figure 1.11b), the increased steric congestion caused by the chelating ligand DME promotes alkylidene formation. A ligand-induced α -abstraction process is also seen in the addition of trimethylphosphine to $\text{W}(\text{NPh})(\text{CH}_2\text{C}(\text{CH}_3)_3)_2(\text{PMe}_3)(\text{Cl})_2$ to give $\text{W}(\text{NPh})(\text{CHC}(\text{CH}_3)_3)(\text{PMe}_3)_2(\text{Cl})_2$ (Figure 1.11c).⁴³

Metal alkylidenes can also be formed by the protonation of metal alkylidynes. An intermolecular example is the addition of two equivalents of HCl to $\text{W}(\text{CC}(\text{CH}_3)_3)(\text{OC}(\text{CH}_3)_3)_3$ to give $\text{W}(\text{CHC}(\text{CH}_3)_3)(\text{OC}(\text{CH}_3)_3)_2(\text{Cl})_2$ (Figure 1.12a).⁴⁴ Related examples include intramolecular and base-catalyzed proton transfer from amido ligands to alkylidynes to give the metal imido alkylidene (Figure 1.12b).⁴⁵

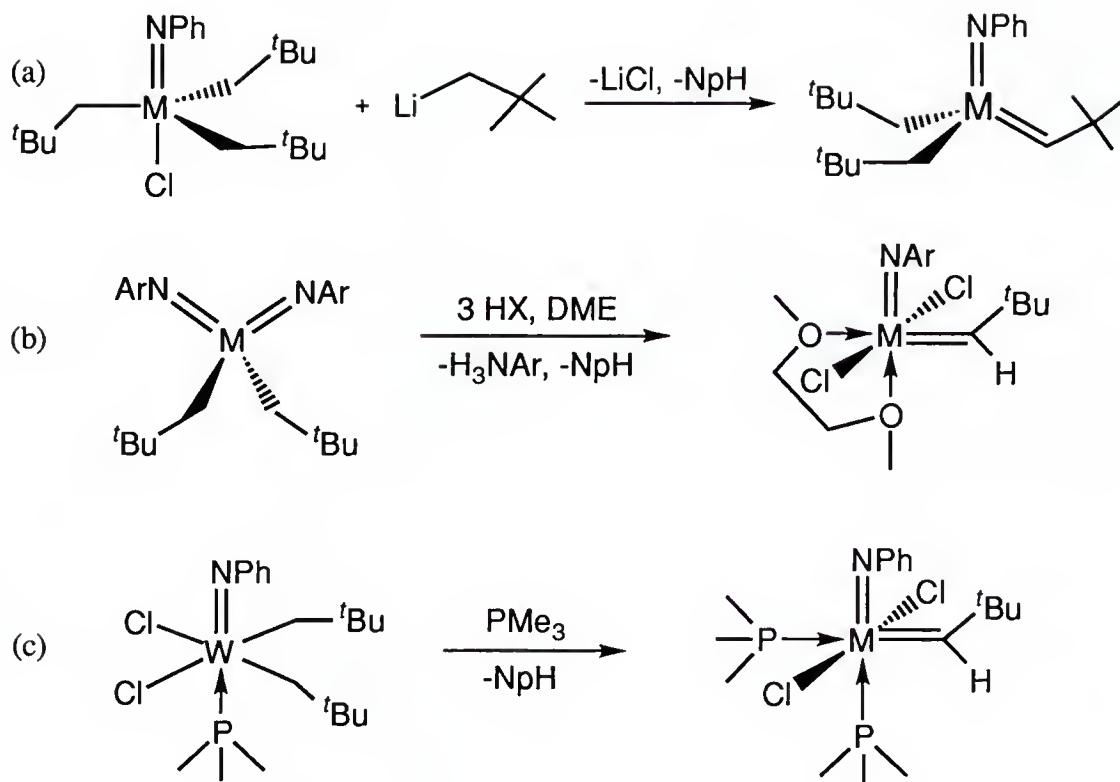


Figure 1.11. Examples of steric-induced (a) and ligand-induced (b, c) α -abstraction reactions.

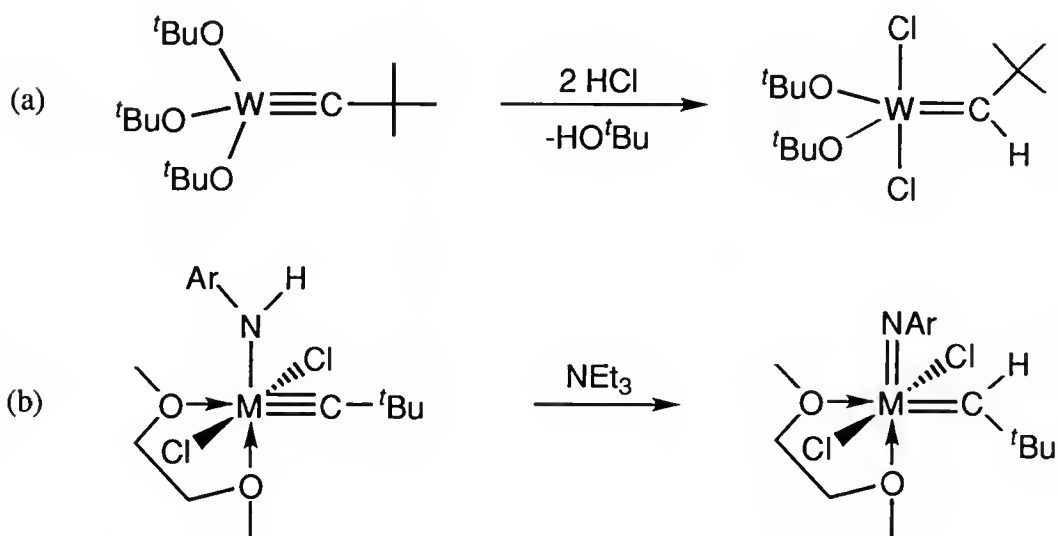


Figure 1.12. Alkylidene formation *via* protonation of an alkylidyne ligand.
a) Intermolecular mechanism with external acid; b) Intramolecular mechanism with amido ligand proton.

Phosphonium ylides, or Wittig reagents, have been used to transfer their carbene moiety to metal complexes. However, ylides do not react with metal oxo complexes to give phosphine oxide and an alkylidene as ylides do with organic carbonyl compounds. Rather, phosphonium ylides react with reduced metal centers to give oxidized metal alkylidenes and free phosphine. An advantage of using ylides is that alkylidene ligands not normally accessible by α -abstraction processes are possible, such as alkylidenes without considerable steric bulk. Examples employing ylides are shown in Figure 1.13 for (a) the formation of the first group 4 metal alkylidene⁴⁶ and (b) the reduction of a tungsten (VI) complex *in situ* to give a chelate-stabilized tungsten (VI) alkylidene complex.^{47,48}

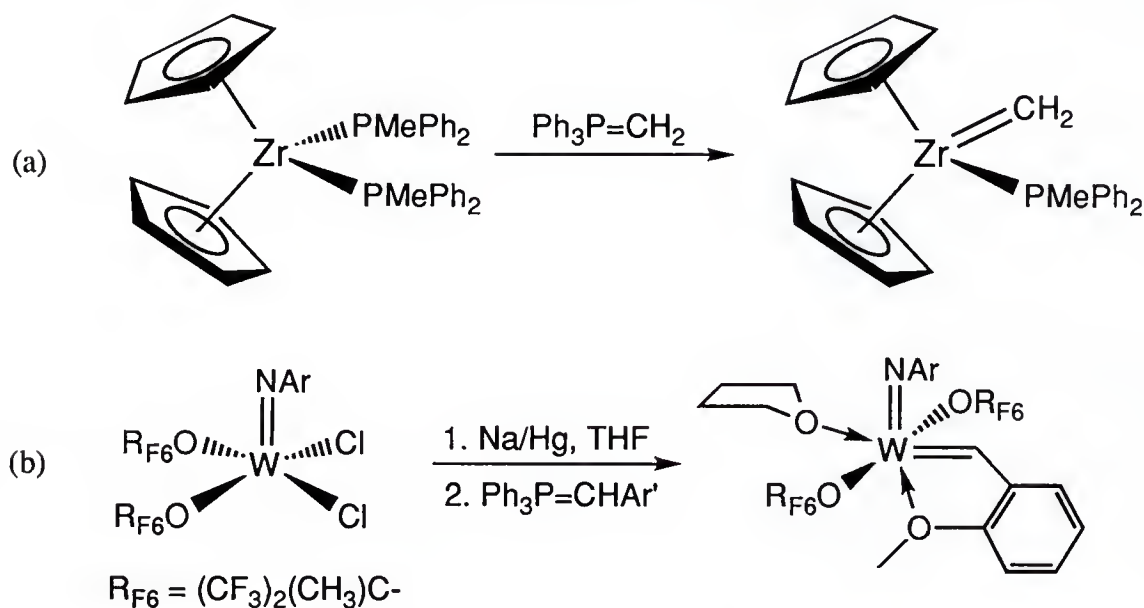


Figure 1.13. Alkylidene complexes *via* phosphoranes. a) The first stable zirconium alkylidene complex; b) Tungsten alkylidene with unique substituent.

Other methods have resulted in the synthesis of metal alkylidene complexes,⁴ but the routes described above are the most applicable to a number of metals and ancillary ligand environments.

¹H NMR spectroscopy often provides the exciting first evidence of new alkylidene complexes.^{4,5,49} Typically, alkylidene α protons resonate at low fields (9-15 ppm) in ¹H NMR spectra. The resonances for α carbons of alkylidene ligands are also found at low

field ranging from 200-350 ppm. Coupling constants, $^1J_{CH}$, range from 70 Hz to 160 Hz. These large differences in chemical shifts indicate the variety of electronic and structural environments in which alkylidene ligands may be found. These differences in NMR data are often correlated to the structure of the metal alkylidene complexes.

X-ray crystallography provides information concerning the metal-carbon bond distances in metal alkylidenes. These distances range from 1.83(2) to 2.14(2) Å for tungsten complexes and from 1.917(5) to 1.989(3) Å for molybdenum complexes.⁴ On average, these bond distances are shorter for electronically unsaturated complexes and longer when other π donor ligands are present. The M-C $_{\alpha}$ -C $_{\beta}$ angle of the alkylidene ligands ranges from 125° to 170°. Bond angles less than 150° are considered to be normal when no agostic interaction of the α -CH bond is present. For bond angles greater than 150°, α agostic interactions are usually responsible and a corresponding decrease in $^1J_{CH}$ (less than 120 Hz) is often observed.

Carbon-hydrogen coupling constants have been used to assign *syn* or *anti* orientations for alkylidene ligands when oxo or imido ligands are present.^{34,36} For electronically and coordinatively unsaturated Mo(NR)(CHR')(OR'')₂ complexes, $^1J_{CH}$ for *syn* rotamers range from 114.0 to 122.5 Hz, and $^1J_{CH}$ for *anti* rotamers range from 142.8 to 155.7 Hz. Such variations in coupling constants are not observed for electronically and coordinatively saturated complexes.³⁵

Reactivity of Metal Alkylidene Ligands

The nucleophilicity of the α -carbon in Schrock-type alkylidene complexes defines their reactivity.³⁸ Alkylidenes react with a range of electrophiles from protons to unsaturated, polar carbonyl-containing compounds. In addition, the heightened reactivity due to the nature of transition metal complexes also activates nonpolar substrates, such as hydrocarbons and olefins.

As metal alkylidynes are protonated by acids, alcohols, and amines to give alkylidenes, alkylidenes are protonated to give metal alkyl complexes. For $\text{Ta}(\text{CHC}(\text{CH}_3)_3)(\text{CH}_2\text{C}(\text{CH}_3)_3)_3$ in Figure 1.14a, the alkylidene ligand is protonated by HCl more readily than the less basic alkyl substituents.³⁸ Legzdins has reported a low-valent, Schrock-type alkylidene complex, $\text{CpMo}(\text{NO})(\text{CHC}(\text{CH}_3)_3)(\text{pyridine})$ (Figure 1.14b), that is protonated by alcohols and amines to give $\text{CpMo}(\text{NO})(\text{CH}_2\text{C}(\text{CH}_3)_3)(\text{ER})$ ($\text{E} = \text{O}, \text{NH}$).⁵⁰ Protonation of an alkylidene is normally not desired synthetically, but in the Legzdins work, the mixed alkyl-amido or -alkoxo complexes are not readily accessible by other routes.

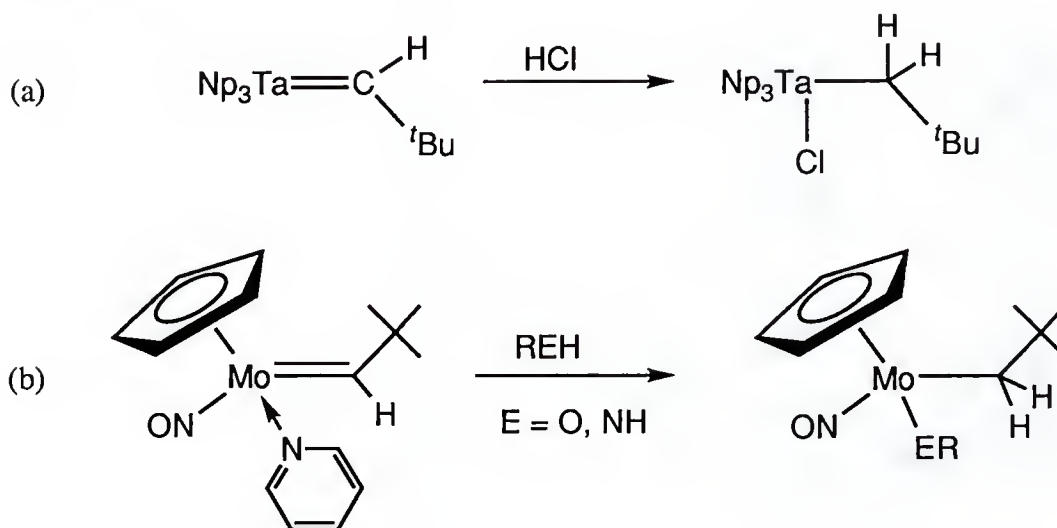


Figure 1.14. Protonation of alkylidene ligands. a) Protonation suggesting greater basicity of alkylidene *versus* alkyl ligands; b) Protonation with alcohols and amines as a synthetic route to mixed alkyl-ER complexes.

Carbon-hydrogen bonds can also be activated by metal alkylidenes.⁴¹ An interesting example that also demonstrates the greater nucleophilicity of an alkylidene versus alkyl ligands is the intramolecular ϵ -C-H activation of an ancillary aryloxide ligand by a tantalum methyl methyldene complex (Figure 1.15).⁵¹

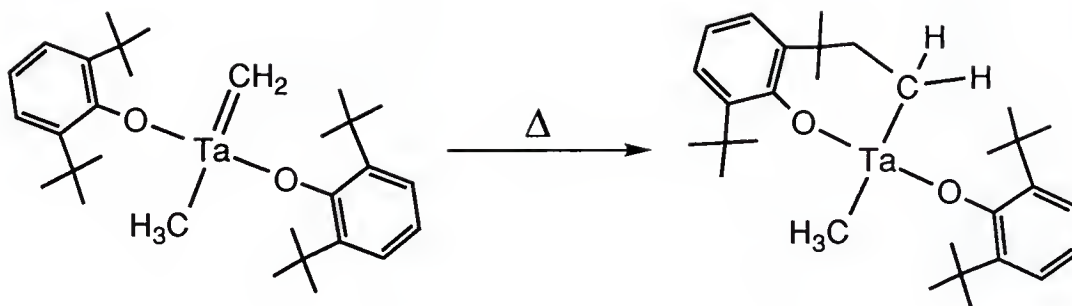


Figure 1.15. Intramolecular ϵ -C-H activation by a methyldiene ligand.

Metal alkylidenes react with carbonyl compounds in a manner similar to Wittig reagents to give metal oxo complexes and olefins. The high electrophilicity of the metal center makes alkylidene transfer possible for substrates not normally activated by phosphonium ylides, such as esters, amides and carbon dioxide. Thus, the Tebbe-Grubbs reagent can be applied to organic synthesis for the methylenation of substrates not amenable to Wittig reactions (Figure 1.16).⁵²

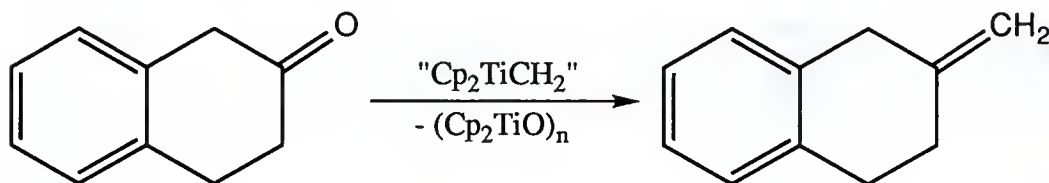


Figure 1.16. Methylenation of a ketone that is susceptible to enolization.

Olefin Metathesis

The considerable interest in metal alkylidene chemistry has been primarily focused on their reactions with olefins. The topics of the olefin metathesis reaction, its use in polymerizations, and the requirements for highly active olefin metathesis catalysts are covered in detail in this section. The olefin metathesis reaction interchanges the carbon fragments of olefins to give new olefins.^{1,2} The reaction has found remarkable application in a number of industrial processes to produce α -olefins and unsaturated polymers. Olefin

metathesis is unobserved as a purely organic transformation, and thus a transition metal catalyst is required (Figure 1.17).⁵³

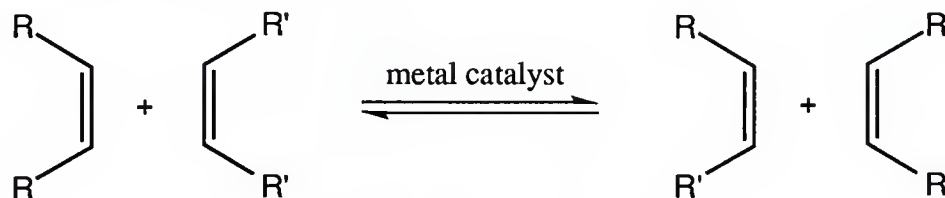


Figure 1.17. Transition metal-catalyzed olefin metathesis.

Olefin metathesis catalysts were discovered as a result of intense research efforts to polymerize α -olefins by Ziegler-Natta catalysts.¹ Early Ziegler-Natta catalysts that gave stereoregular, unsaturated polymers from α -olefins were composed of transition metal halide compounds and Lewis acid cocatalysts, such as alkyl aluminum compounds. Attempts to extend Ziegler-Natta chemistry to group 6 metals resulted in the first olefin metathesis catalysts.

The nature of the catalytic species in these early catalysts and the mechanism of the reaction were unknown for years even though olefin metathesis was highly exploited by industry. After years of observations of product ratios, reaction kinetics, and model studies from several researchers,⁵⁴ Hérrison and Chauvin proposed that the active catalytic species consisted of a metal alkylidene and that the mechanism involved the fragmentation of reactant olefins to give product olefins.³ This non-pairwise mechanism is shown below.

The non-pairwise mechanism, shown in Figure 1.18, consists of a series of equilibria involving (a) coordination of an olefin to a metal alkylidene complex, the (b) formation and (c) constructive decomposition of a metallacyclobutane, and (d) the dissociation of the new olefin from a new metal alkylidene complex. The formation of a reactive metal alkylidene complex in some classical catalyst mixtures results from the alkylation of the metal center by the cocatalyst and subsequent α -abstraction to give a metal-carbon double bond.

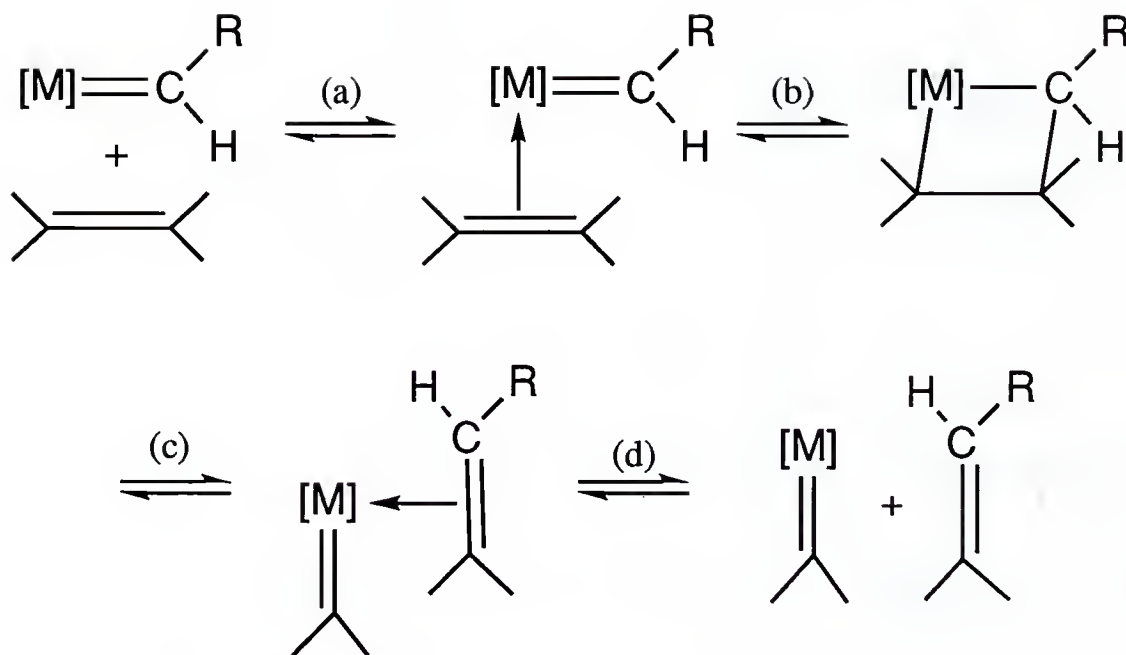


Figure 1.18. The non-pairwise mechanism for olefin metathesis.

Polymers can be synthesized by olefin metathesis in two distinct ways: the ring-opening metathesis polymerization (ROMP) of cyclic olefins (Figure 1.19)¹ and acyclic diene metathesis (ADMET) polymerization (Figure 1.20).⁵⁵ Both reactions result in linear, unsaturated polymers, but they differ greatly from a synthetic viewpoint.

The ROMP reaction involves the metathesis of strained cyclic olefins, and it is the relief of ring strain that drives the reaction to completion. The advantages of ROMP include a chain-growth polymerization mechanism in which the growing polymer chain never dissociates from the metal center in well-behaved systems. This results in rapid increases in molecular weight and narrow molecular weight distributions.

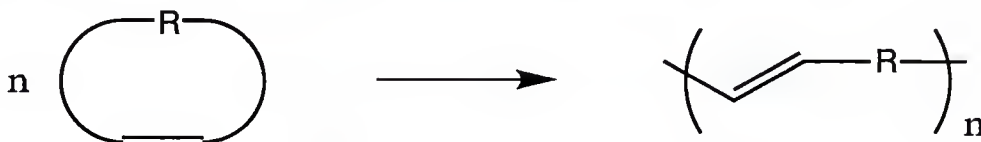


Figure 1.19. Ring-opening metathesis polymerization (ROMP).

Acyclic diene metathesis differs from ROMP in that ADMET is a step-growth, condensation polymerization. The equilibrium of this condensation polymerization is driven to polymer by the removal of small, low-boiling by-products, such as ethylene. A consequence of the step-growth mechanism is that high molecular weights are only achieved at quantitative conversion and polydispersities are statistically broad. As a result, side reactions must be eliminated and monomer purity is imperative.⁵⁶



Figure 1.20. Acyclic diene metathesis (ADMET) polymerization.

ADMET polymerization was not viable in the classical catalyst systems because of side reactions such as vinyl addition, but by employing the highly active, Lewis acid-free metathesis catalysts reported by Schrock, the quantitative conversion of monomer to polymer was first achieved by the Wagener research group at the University of Florida.^{57,58} The major advantage of ADMET over its ROMP counterpart is that strained cyclic monomers are not necessary, and a wider array of monomers with a variety of functionalities are suitable candidates for polymerizations. Also, it has been shown that depolymerization of unsaturated polymers in the presence of excess olefins is possible by nature of the reversible equilibrium.^{59,60}

As mentioned, the success of ADMET depended greatly on the use of highly active, Lewis acid-free metathesis catalysts of the form $\text{M}(\text{CHR})(\text{NAr})(\text{OR}_{\text{F6}})_2$ ($\text{M} = \text{Mo}, \text{W}$; $\text{R} = t\text{-Bu}$; $\text{Ar} = 2,6\text{-(}i\text{-Pr)}_2\text{C}_6\text{H}_3$; $\text{OR}_{\text{F6}} = \text{OC}(\text{CH}_3)(\text{CF}_3)_2$) (Figure 1.21). These new metathesis catalysts were the dawn in a new era in catalyst activity and design, and a discussion of their development provides considerable insight into some essential elements of active metathesis catalysts.⁶¹

The first step in olefin metathesis is the coordination of an olefin to the metal center, and this necessitates a coordinatively unsaturated metal alkylidene complex. Earlier

catalysts were five or six coordinate to avoid dimerization of the complexes and required Lewis acids to open a coordination sight.^{62,63} The use of dianionic oxo or imido ligands would lower the coordination number to four, and with imido ligands, a sterically demanding substituent could deter dimerization. Thus, Schrock employed the bulky 2,6-diisopropyl imido ligand to shield the metal center and maintain a low coordination number and a high oxidation state.⁶¹ The use of the π -donating imido ligand is also advantageous because of its ability to stabilize the catalytic intermediates as a 'spectator ligand'.¹²

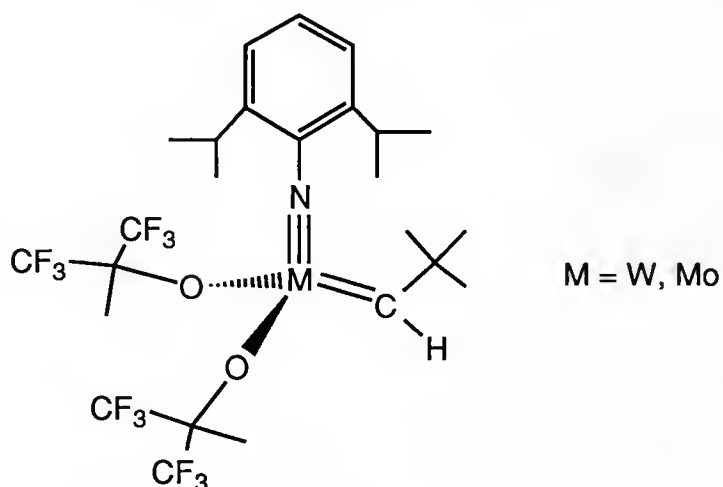


Figure 1.21. The Lewis acid-free metathesis catalyst.

Active metathesis catalysts seem to require π -donation from the other ancillary ligands. Alkoxide ligands have an advantage over halide ligands due to their enhanced stabilization of intermediates by π -donation.⁶⁴ On the other hand, it is necessary to maintain an electrophilic metal center to enhance olefin binding. Schrock employed a series of relatively bulky t-butoxides that were fluorinated to increase the electrophilicity of the metal.⁶⁵ The metathesis activities depend dramatically on the balance of electronic and steric properties of the alkoxide ligand employed, following the order $\text{OC}(\text{CH}_3)(\text{CF}_3)_2 > \text{OC}(\text{CH}_3)_2(\text{CF}_3) > \text{OC}(\text{CF}_3)_3 > \text{OC}(\text{CF}_3)_2(\text{CF}_2\text{CF}_2\text{CF}_3) \gg \text{OC}(\text{CH}_3)_3$.

There are numerous differences in the details between the molybdenum and tungsten analogues of Schrock's catalyst. Two of the more salient differences between the metals are a greater tolerance to substrate functionality for the molybdenum analogue and

differences in their preference for terminal versus internal olefins. The tolerance of functionalities for molybdenum is attributed to the molybdenum-carbon double bond being less polar than that of tungsten.⁴² For ADMET, these functional groups include amines, ethers,⁶⁶ thioethers,⁶⁷ ketones, esters,⁶⁸ carbonates,⁶⁹ carbosilanes⁷⁰ and carbosiloxanes.⁷¹ Metathesis activity for internal olefins is greater for tungsten while metathesis activity of terminal olefins is greater for molybdenum.⁴² As a result, ADMET polymerizations utilize the molybdenum catalyst and depolymerizations utilize the tungsten catalyst.^{60,68} Elimination of the non-productive, internal olefin metathesis reactions would greatly enhance the rate of ADMET.

The success of Schrock's catalysts in ADMET polymerizations has led to a wide range of new polymers not previously attainable with ROMP monomers. However, drawbacks still exist, and catalysts with greater ADMET reactivity and applications are desired. The drawbacks most importantly are due to the thermal sensitivity of the catalyst during polymerizations. Since ADMET is a step polymerization, the polymerization is preferably performed in neat monomer in order to maximize the concentration of reactive end groups. As a result of this condition, solubility problems arise for the growing polymer. Neat poly(octenamer) solidifies at ambient temperature after only reaching a degree of polymerization of 11.⁶⁸ Heating the reaction would increase solubility or essentially allow the reaction to take place in the melted phase. In addition, step polymerizations are inherently slower than chain polymerizations, and increasing the temperature would accelerate the overall reaction.

Chelated Transition Metal Alkylidene Complexes

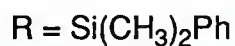
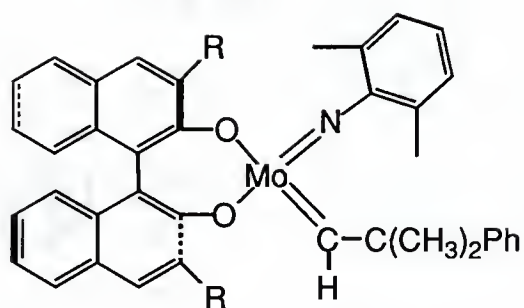
The problems associated with catalyst sensitivity can be addressed by the use of ancillary chelating ligands. Chelating ligands are widely used for the stabilization of transition metal complexes.⁵ The kinetic advantage of the chelate effect reduces the likelihood of certain decomposition pathways, such as ligand substitution, protonolysis and

dimerization, and thus increases the stability of a complex over a wider range of temperatures and conditions. As a consequence of the increased stability, catalytic activity often suffers. The increased hapticity, or coordination number, of the ligand can occupy vacancies necessary for substrate coordination. Also, the chelating ligand decreases the fluxionality and alters the coordination geometry of the complex, and certain rearrangements or related processes may be critical to the mechanism of catalysis. Because a balance between stability and reactivity is necessary in the design of d^0 transition metal alkylidenes, it is desirable to have chelating ligands of high charge and low coordination number.

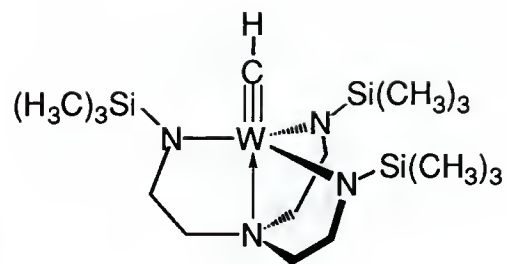
In varying the hapticity and charge of the ligand system in neutral group 6 metal imido alkylidene complexes, the ancillary ligands must have a combined charge of -2. Ideally, a bidentate, dianionic chelating ligand would satisfy the d^0 requirement and result in the lowest possible coordination number of four. Chelating ligands that are neutral or monoanionic only raise the total coordination number and the electron count at the metal center. Examples of a variety of hapticity/charge combinations are reported in the literature and are shown in Figure 1.22.⁷²⁻⁷⁹

Of particular note are the examples using hydridotris(pyrazolyl)borate (Tp, Figure 1.22e)⁷⁶⁻⁷⁸ and N,N'-bis(trimethylsilyl)-*o*-phenylenediamine (TMS₂pda, Figure 1.22f) ligands.⁷⁹ Both ligands are the focus of study in this dissertation, and the previous work from our research group using these ligands is described below.

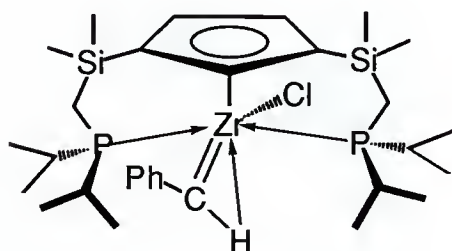
Polypyrazolylborates have found wide application as chelating ligands since their synthesis was described in 1967.^{80,81} This class of ligand has been used with virtually every metal and metalloid in the periodic table. A recent review by their discoverer Swiatoslaw Trofimenko references 460 papers from 1984 to 1993!⁸² Mostly the tridentate, monoanionic ligands have been used with low-valent transition metals,⁸² but the Boncella research group reported the ligands' first application to tungsten (VI) compounds in 1991



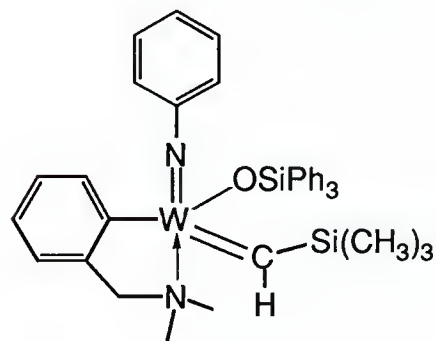
a. bidentate, dianionic



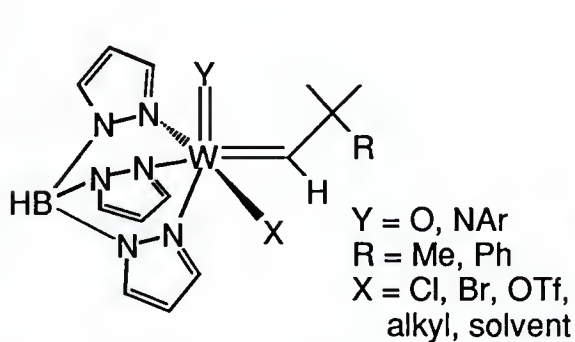
b. tetradentate, trianionic



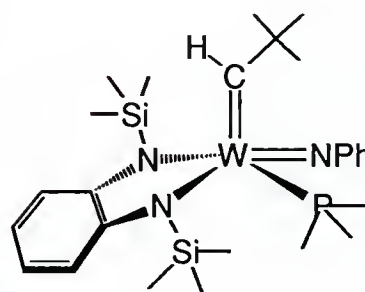
c. pentadentate, monoanionic



d. bidentate, monoanionic



e. tridentate, monoanionic



f. bidentate, dianionic

Figure 1.22. Multidentate ligands used in the stabilization of metal-carbon multiple bonds (hapticity/charge).

a) Binaphtholate (2/-2)

b) Tris(amidoethyl)amine (3/-3)

c) Bis(phosphino)cyclopentadienide (5/-1)

d) Phenylaminomethane (2/-1);

e) Hydridotris(pyrazolyl)borate, Tp (3/-1)

f) N,N'-bis(trimethylsilyl)phenylenediamide, TMS₂pda (2/-2).

to give $\text{Tp}'\text{W}(\text{CC}(\text{CH}_3)_3)\text{Cl}_2$ and $\text{Tp}'\text{W}(\text{CHC}(\text{CH}_3)_3)(\text{O})\text{Cl}$ (Tp' = hydridotris(3,5-dimethylpyrazolyl)borate).⁷⁶

The Tp and Tp' tungsten alkylidene complexes synthesized by the Boncella group have a generalized formula $\text{Tp}^*\text{W}(\text{CHR})(\text{E})(\text{X})$ ($\text{Tp}^* = \text{Tp}, \text{Tp}'$; $\text{R} = \text{C}(\text{CH}_3)_3$, $\text{C}(\text{CH}_3)_2\text{Ph}$; $\text{E} = \text{O}, \text{NPh}, \text{N}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)$; $\text{X} = \text{Cl}, \text{Br}, \text{OSO}_2\text{CF}_3$, alkyl, donor solvent). These complexes exhibit exceptional air, moisture, and thermal stabilities in comparison to the Schrock catalysts. Their high stability is a result of electronically saturated, six-coordinate metal centers imparted by the facially bound, tridentate ligand. The increased stability allows for synthetic manipulations of the complexes not available to the more reactive Schrock catalysts. Highly electrophilic, cationic compounds can be synthesized,⁷⁸ and detailed rotamer isomerization studies were possible.³⁵ However, the saturated metal centers did not result in the complexes being active metathesis catalysts.⁸³ Catalytic activity for the ROMP of cyclooctene and norbornylene and ADMET oligomerizations was induced by the addition of the Lewis acid AlCl_3 , but the active catalytic species remains unknown.

In order to allow metathesis activity without Lewis acids while still gaining advantages from chelating ligands, VanderLende and Boncella used the sterically demanding N,N'-bis(trimethylsilyl)-*o*-phenylenediamine (TMS_2pda) ligand to stabilize the metal alkylidene complex (Figure 1.23).^{79,84} The five-coordinate TMS_2pda tungsten

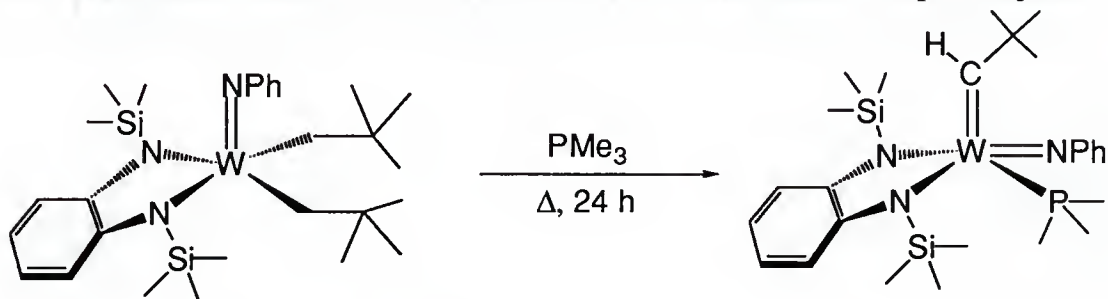


Figure 1.23. Synthesis of the TMS_2pda tungsten alkylidene complex.

alkylidene complex prepared was found to be an active ROMP catalyst following the dissociation of phosphine ligand. The complex was found to be thermally stable for days

in toluene at 110 °C. However, due to the nature of the silicon-nitrogen, tungsten-amido, and tungsten-alkylidene bonds, the complex is extremely air and moisture sensitive.

In continuing research in the area of chelate-stabilized transition metal alkylidene complexes, two projects were undertaken using the Tp and the TMS₂pda ligand systems. Molybdenum analogues of the Tp tungsten compounds were prepared. Tungsten and molybdenum complexes often behave quite similarly with the exceptions mentioned above. Because the Tp tungsten compounds were active metathesis catalysts in the presence of Lewis acids, it was hoped that the advantages of molybdenum might be gained pertaining to the higher affinity of terminal olefins and tolerance of functionality. The chemistry of Tp molybdenum imido alkylidene complexes is covered in Chapter Two. The chapter contents have either previously appeared in refereed journals or are currently in press.⁸⁵⁻⁸⁷

Attempts were also made to extend the use of TMS₂pda to molybdenum. Regrettably, the lower oxidation potentials for molybdenum versus tungsten resulted in the reduction of molybdenum to presumably *d¹* decomposition products. However, the TMS₂pda tungsten alkylidene complex and its precursors provided rich opportunities for the synthesis of chelated tungsten alkyl and hydride complexes.⁸⁴ As a result of the synthetic observations, it became necessary to study the kinetics and mechanisms of the formation of these new TMS₂pda tungsten complexes. Close examination of the system has revealed that the TMS₂pda ligand is not merely ancillary and innocuous. Chapter Three details the observations gathered to date and mechanistic relationships inferred between the TMS₂pda tungsten complexes.

CHAPTER 2

MOLYBDENUM IMIDO ALKYLIDENE COMPLEXES STABILIZED BY HYDRIDOTRIS(PYRAZOLYL)BORATE

The success of using hydridotris(pyrazolyl)borate, Tp, to stabilize tungsten complexes led to the extension of this chemistry to molybdenum. Reasons for exploring the use of molybdenum are more than just its similarity to tungsten. As previously mentioned, molybdenum alkylidene complexes are typically more tolerant of functionalized substrates and show higher metathesis activity for terminal olefins than tungsten complexes. Though the reaction chemistry of molybdenum and tungsten parallels one another in most cases, d^0 molybdenum complexes are often observed to be less stable to reduction than tungsten. As a result, some starting materials available for tungsten are not as readily accessible for molybdenum.

The molybdenum imido alkylidene complex, $\text{Mo}(\text{CHC}(\text{Me})_2\text{Ph})(\text{NAr})(\text{OTf})_2(\text{DME})$, reported by Schrock is a suitable starting material to enter into the chemistry of chelated hydridotris(pyrazolyl)borates. Stabilizing molybdenum imido alkylidene complexes with Tp has led to chemistry previously seen with tungsten, including the synthesis of cationic complexes and ROMP catalyst precursors. In addition, several new complexes and transformations not seen with tungsten have been observed, and analysis of the series of new compounds has offered further insight to the nature of metal imido alkylidenes in the octahedral environment of the Tp ligand. The contents of this chapter are subdivided into new neutral Tp molybdenum complexes, synthetic schemes for cationic compounds, the *trans* influence imparted on the Tp pyrazolyl rings by ligands, rotational isomerization studies, and the olefin polymerization activity of these new complexes.

Neutral Molybdenum Imido Alkylidene Complexes

The chelating Tp ligand provides an excellent opportunity to substitute alkylidene complexes with different ancillary ligands. This section describes the synthesis, characterization and reactivity of neutral molybdenum imido alkylidene complexes beginning with $\text{TpMo}(\text{CHC}(\text{Me})_2\text{Ph})(\text{NAr})(\text{OTf})$ (**1**) which proved to be a useful starting material that is readily available.

Synthesis of $\text{TpMo}(\text{CHC}(\text{Me})_2\text{Ph})(\text{NAr})(\text{OTf})$ (**1**)

The reaction of one equivalent of KTp with $\text{Mo}(\text{CHC}(\text{Me})_2\text{Ph})(\text{NAr})(\text{OTf})_2(\text{DME})$ ⁴² in THF at ambient temperature results in the rapid formation of $\text{TpMo}(\text{CHC}(\text{Me})_2\text{Ph})(\text{NAr})(\text{OTf})$ (**1**, eq 1) which is obtained as bright yellow needles from pentane. Compound **1** is stable in air as a solid for one month with no evidence of decomposition by ^1H NMR and it decomposes in air at 155 °C. The chelating ability of the Tp ligand and the increased steric bulk at the metal,⁸⁸ as well as the formal 18 electron count at the metal, are responsible for the robust nature of compound **1**.

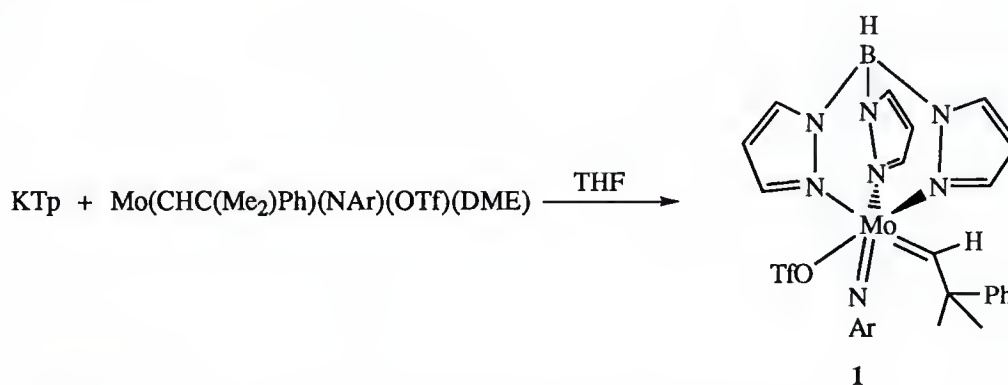


Figure 2.1. Synthesis of $\text{TpMo}(\text{CHC}(\text{Me})_2\text{Ph})(\text{NAr})(\text{OTf})$ (**1**).

The ^1H NMR spectrum (Figure 2.2) of compound **1** at 22 °C is complicated by the chirality of the compound, resulting in nine distinct pyrazole proton resonances and diastereotopic methyl resonances for the neophylidene ligand and for the isopropyl groups

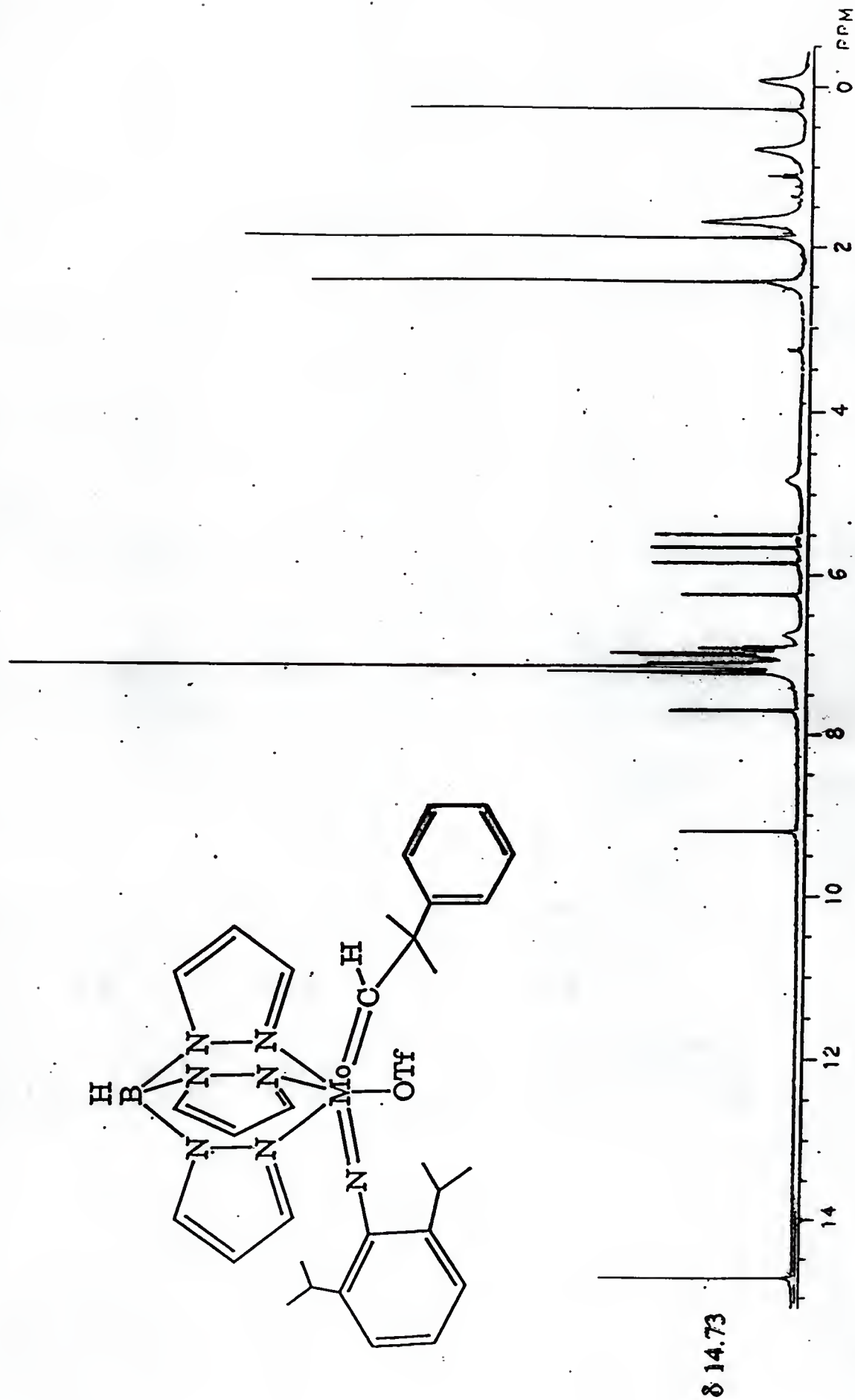


Figure 2.2. ^1H NMR spectrum of $\text{TpMo}(\text{CHO}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{OTf})$ (1).

of the aryl imido ligand. The proton signals of the isopropyl groups of the aryl imido ligand are broad, suggesting hindered rotation about the nitrogen-aryl bond. Variable temperature NMR measurements were used to measure a barrier to rotation of 15 kcal/mole for the nitrogen-carbon bond. The solution structure was determined by ^1H difference NMR experiments, and found to be the *syn* isomer in which the alkylidene $\text{C}(\text{Me})_2\text{Ph}$ group is oriented towards the imido ligand.³⁴ The triflate ligand is covalently bound to the metal center, demonstrated by strong characteristic IR absorptions at 1202 and 633 cm^{-1} assigned to the S=O stretches of the triflate ligand.⁸⁹ Crystals of **1** suitable for x-ray diffraction studies were obtained by slowly cooling a saturated hexane solution of **1** from 40 °C to ambient temperature.

Crystal Structure of $\text{TpMo}(\text{CHC}(\text{Me})_2\text{Ph})(\text{NAr})(\text{OTf})$ (**1**)

There are several pertinent features of the structure of **1** (Figure 2.3) that are analogous to features of other structurally characterized Tp or imido-alkylidene complexes.⁴² Selected bond distances and angles are given in Table 2.1. The coordination geometry around the molybdenum atom in **1** is that of a distorted octahedron. The geometric constraints of the facially-bound Tp ligand force the neophylidene, aryl imido, and triflate ligands to be mutually *cis*. The N-Mo bond lengths of the chelating pyrazolyl rings [Mo-N1, 2.311(8)Å; Mo-N3, 2.167(8)Å; Mo-N5, 2.311(9)Å] are consistent with the decreasing *trans* influence of the ligands imido $\approx$ alkylidene > triflate.

The *cis* orientation of the aryl imido ligand and alkylidene ligand allows for maximum $d\pi\text{-}p\pi$ bonding between the molybdenum and the multiply bonded ligands. The Mo-N bond length of 1.753(8) Å and Mo-N-C11 bond angle of 170.9(7)° are within the normal ranges for molybdenum imido complexes in which the molybdenum-nitrogen bond can be considered to be triply bound with the lone pair of the nitrogen donating to an empty $d\pi$ orbital of the d^0 molybdenum atom.

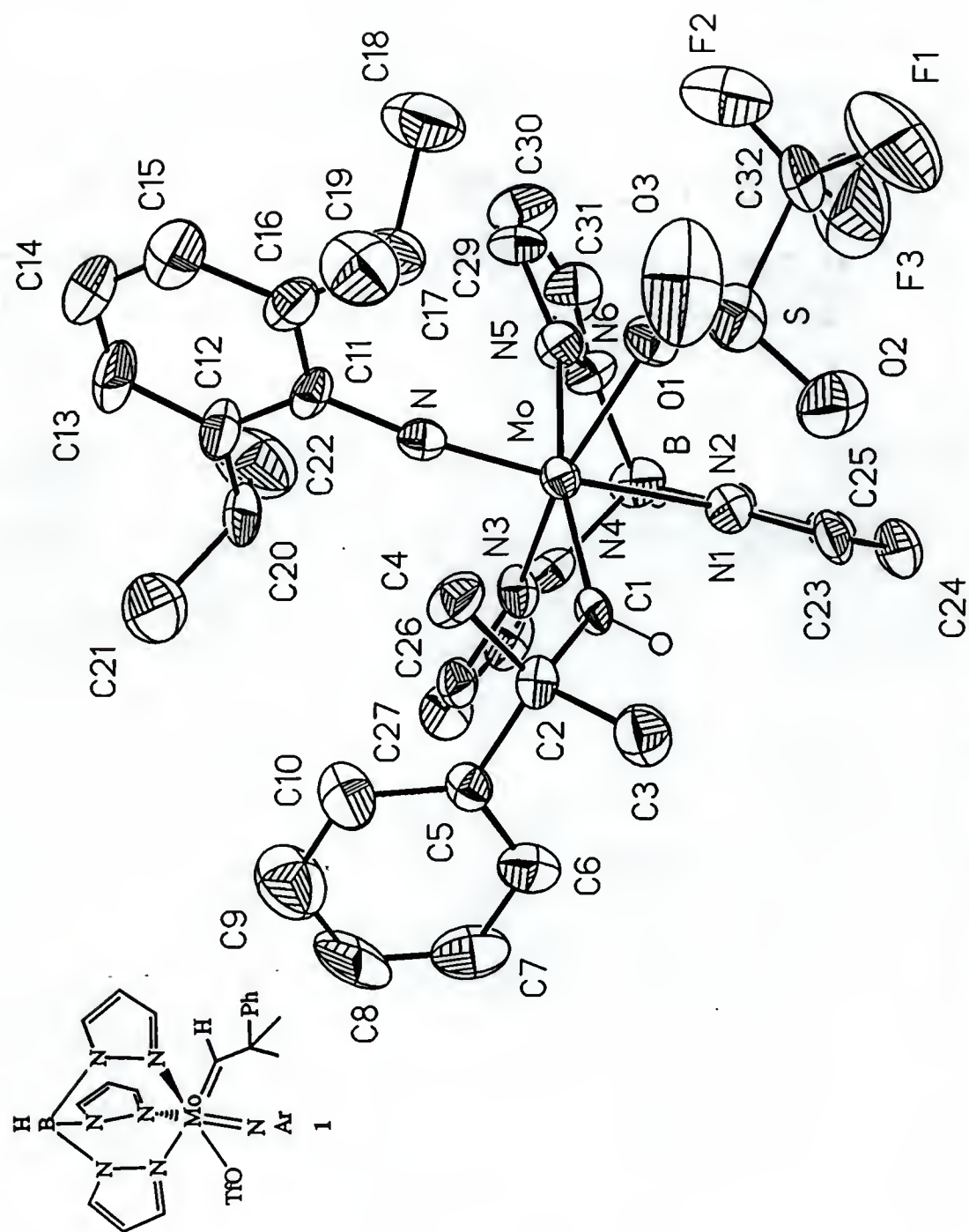


Figure 2.3. Thermal ellipsoid plot of $\text{TpMo}(\text{CHC}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{OTf})$ (1).

Table 2.1: Selected Bond Lengths (Å) and Angles (°) for compound **1**.

<u>1</u>	<u>2</u>	<u>3</u>	<u>1-2</u>	<u>1-2-3</u>
O1	Mo	N	2.121(7)	96.5(3)
O1	Mo	N1		84.0(3)
O1	Mo	N3		158.8(3)
O1	Mo	N5		81.7(3)
N	Mo	N1	1.753(8)	170.8(3)
N	Mo	N3		99.8(4)
N	Mo	N5		92.2(3)
N	Mo	C1		100.5(4)
N1	Mo	N3	2.311(8)	77.7(3)
N1	Mo	N5		78.8(3)
N1	Mo	C1		88.5(4)
N3	Mo	N5	2.167(8)	84.3(3)
N3	Mo	C1		91.5(4)
N5	Mo	C1	2.311(9)	167.2(4)
C1	Mo	O1	1.949(10)	98.7(4)
Mo	O1	S		141.5(5)
C11	N	Mo	1.396(12)	170.9(7)
C2	C1	Mo	1.501(14)	139.6(8)

The Mo-C1 bond length, 1.949(10) Å, lies within the expected range for molybdenum-carbon double bonds. The -CMe₂Ph group of the alkylidene is in the *syn* or *s-cis* orientation with respect to the imido ligand. This *syn* orientation for the neophylidene ligand is also present in the solution structure as determined by ¹H difference NMR spectra. The steric congestion imposed by the *syn* orientation of the neophylidene ligand results in the aryl ring of the imido ligand being situated perpendicular to the plane containing atoms N, Mo, C1 and C2. The acute angle of the alkylidene proton with molybdenum [Mo-C1-H1 = 104.(5)°] is not likely a result of any agostic interaction since the molybdenum atom is coordinatively and electronically saturated, but rather due to the opening of the Mo-C1-C2 angle caused by the steric constraints of the coordination sphere.

The Mo-OTf bond distance of 2.121(7) Å is long compared to the Mo-OMe bond length, 1.960(7) Å, in the related compound TpMo(ChC(Me)₂Ph)(NAr)(OMe) (**4**) *vide infra*. However the Mo-OTf bond length is within the range for covalently bound triflate

ligands.⁹⁰ The presence of a bound triflate ligand was also supported by the presence of characteristic S=O stretches in the infrared spectrum of **1**. Though the triflate anion is often thought of as being non-coordinating, the high electrophilicity of the metal center and the ability of the Tp ligand to efficiently polarize metal orbitals into an octahedral array⁸⁸ lead to the interaction between the metal center and the relatively ionic, poor π -donating triflate ligand. The triflate ligand is slightly disordered which can be described as a distortion of the Mo-O1-S angle propagating into increasing thermal parameters for O2, O3, C32, F1, F2 and F3 atoms.

Synthesis of $\text{TpMo}(\text{CH}_2\text{C}(\text{Me})_2\text{Ph})(\text{NAr})(\text{O})$ (**2**)

Compound **1** in THF is stable in the presence of H_2O over a period of 24 hours. However, when a wet Et_2O solution of **1** is passed over a column of alumina, a small amount of $\text{TpMo}(\text{CH}_2\text{C}(\text{Me})_2\text{Ph})(\text{NAr})(\text{O})$ (**2**) was observed by ^1H NMR. Stirring compound **1** in a slurry of Florisil in Et_2O and H_2O for 24 hours afforded an orange solution of compound **2** which can be recrystallized from pentane to give orange crystals. This result compares with a previously reported reaction by our group in which a tungsten alkylidyne complex, $\text{Tp}'\text{W}(\text{CCMe}_3)\text{Cl}_2$, is converted to the tungsten alkylidene complex, $\text{Tp}'\text{W}(\text{CHCMe}_3)\text{OCl}$, by stirring over alumina.⁷⁶ Also, the reaction of compound **1** with one equivalent of CsOH in THF gave a quantitative yield of **2**. Heating **2** in excess PMe_3 for 5 days at 65°C showed no reaction by ^1H NMR and no evidence of phosphine oxide or phosphazine.

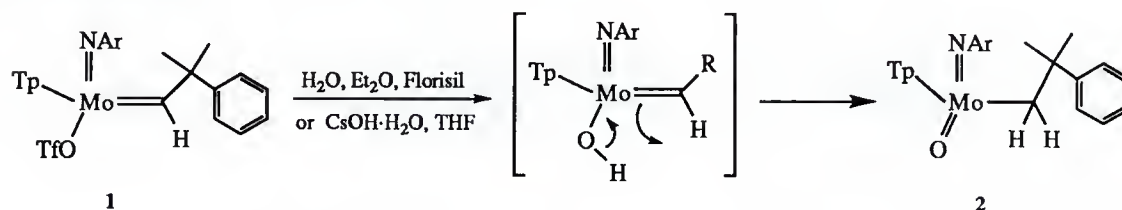


Figure 2.4. Syntheses of $\text{TpMo}(\text{CH}_2\text{C}(\text{Me})_2\text{Ph})(\text{NAr})(\text{O})$ (**2**).

The distinctive features of the ^1H NMR spectrum (Figure 2.5) of compound **2** are the presence of an AB quartet corresponding to the diastereotopic protons of the $\text{CH}_2\text{C}(\text{Me})_2\text{Ph}$ ligand and the loss of the downfield alkylidene resonance of the alkylidene proton of **1**. The isopropyl groups of the aryl imido ligand are responsible for a broad multiplet due to the methine protons and two slightly broadened doublets due to the methyl protons indicating that the N-Ar bond rotates more freely than that of compound **1**. The molybdenum-oxygen bond appears as a strong absorption at 896 cm^{-1} in the IR spectrum which is within the normal range for molybdenum oxo compounds containing additional multiply bonded ligands.⁴

One possible mechanism for the formation of **2** is the displacement of the triflate ligand by hydroxide to form an unobserved hydroxy-alkylidene species (Figure 2.4). Subsequent proton transfer from the oxygen to the α -carbon of the alkylidene results in the favorable formation of the strong molybdenum-oxygen triple bond. The previously reported tungsten analogue of **2** was prepared by the protonation of $\text{TpW}(\text{CHC}(\text{Me})_2\text{Ph})(\text{NAr})(\text{CH}_2\text{C}(\text{Me})_2\text{Ph})$ by HBF_4 in the presence of H_2O to give $[\text{TpW}(\text{NHAr})(\text{O})(\text{CH}_2\text{C}(\text{Me})_2\text{Ph})][\text{BF}_4]$ followed by deprotonation by NEt_3 .⁷⁸ This result suggests an acid-catalyzed mechanism for the formation of **2** in the Florisil preparation.

Crystal Structure of $\text{TpMo}(\text{CH}_2\text{C}(\text{Me})_2\text{Ph})(\text{NAr})(\text{O})$ (**2**)

The structure of compound **2** was determined by X-ray diffraction methods and a thermal ellipsoid plot is found in Figure 2.6. Selected bond distances and angles are given in Table 2.2. The structure consists of well-separated molecules with a pseudooctahedral coordination geometry about the metal. The geometric constraints of the facially-bound Tp ligand force the oxo, imido, and alkyl ligands to be mutually *cis*, with a O-Mo-N angle of $103.68(9)^\circ$.¹⁵ The N-Mo bond lengths of the chelating pyrazole rings range from

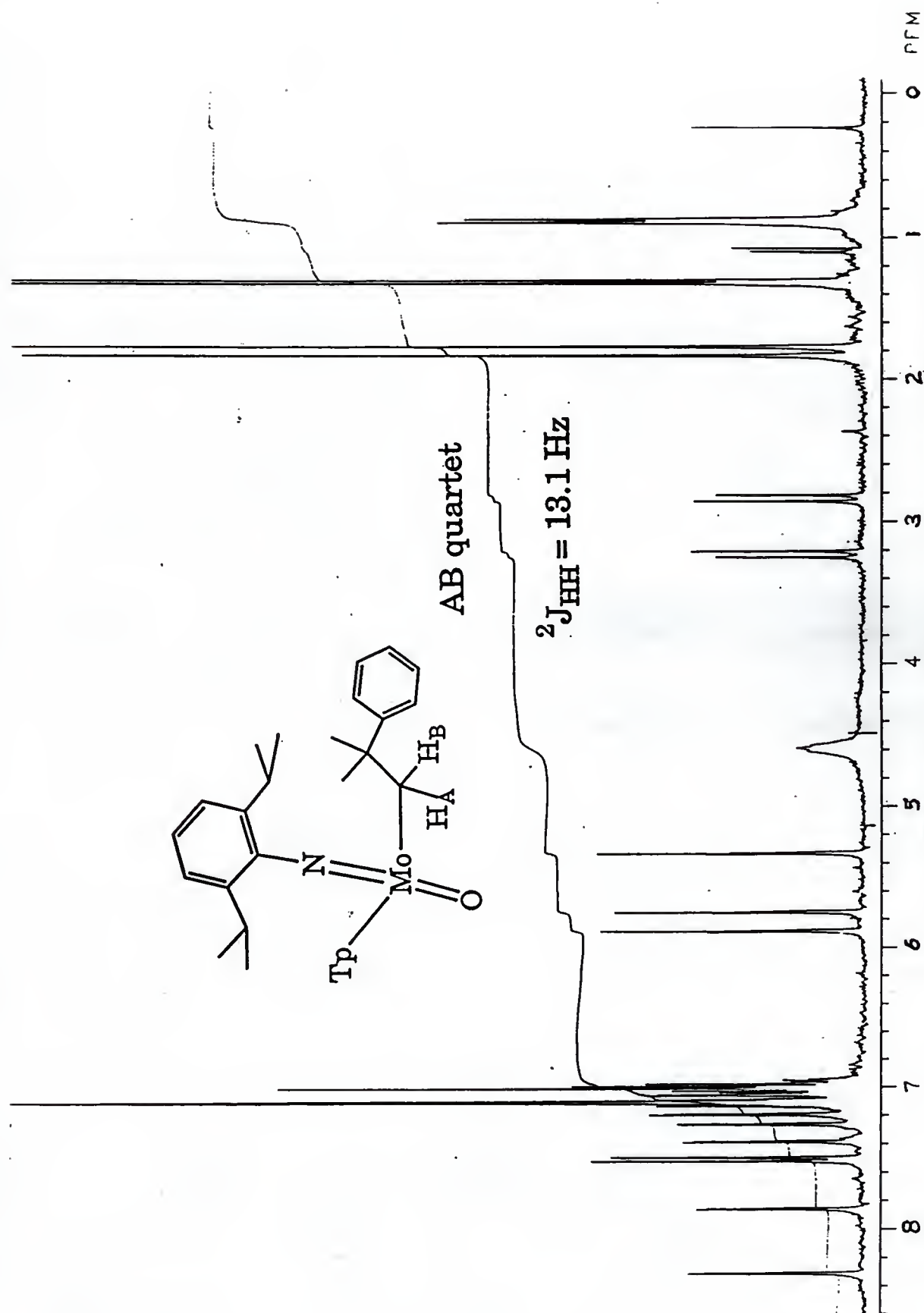


Figure 2.5. ^1H NMR spectrum of $\text{TpMo}(\text{CH}_2\text{C}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{O})$ (2).

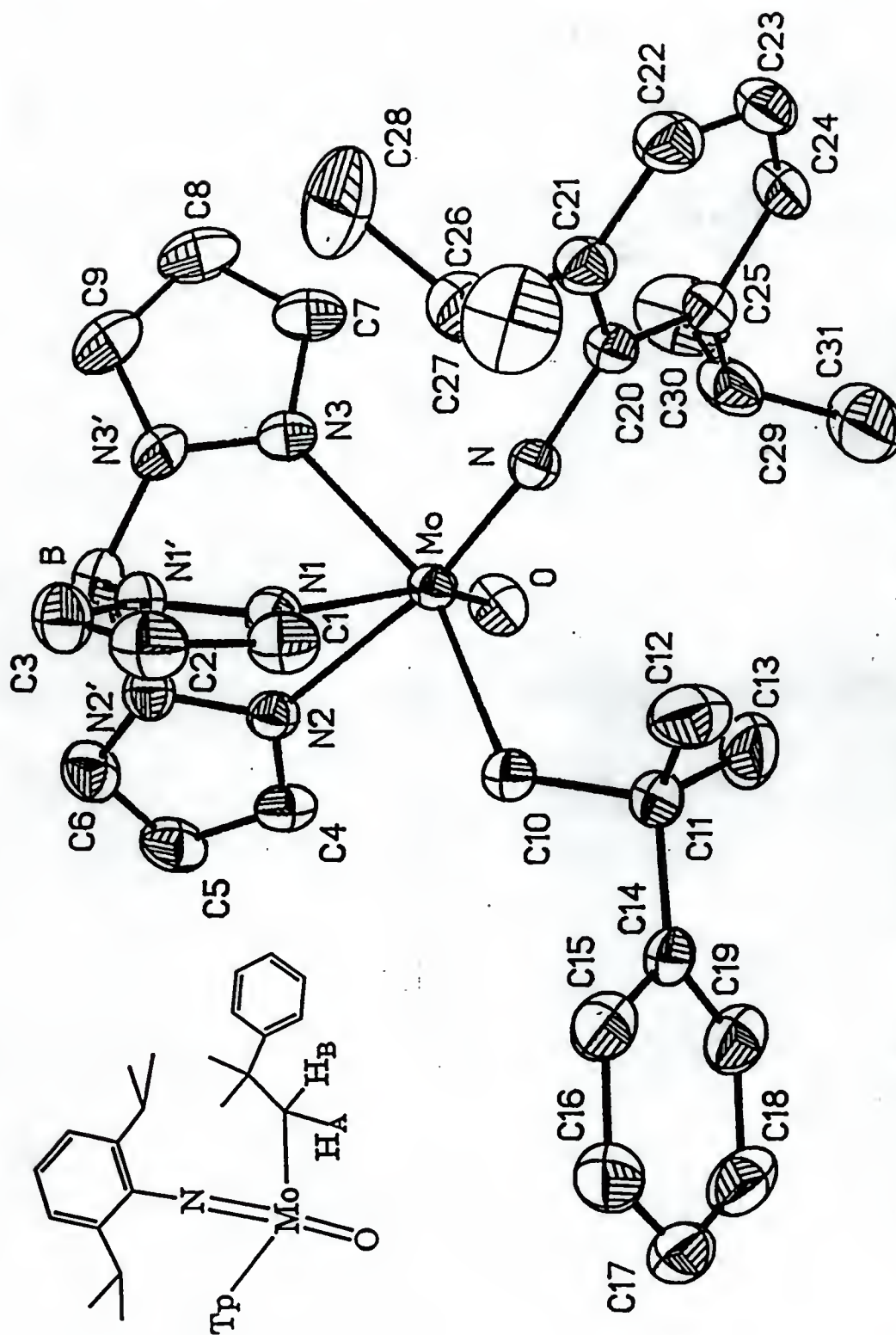


Figure 2.6. Thermal ellipsoid plot of $\text{TpMo}(\text{CH}_2\text{C}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{O})$ (**2**).

2.379(2)Å to 2.207(2)Å and are consistent with the decreasing *trans* influence of the ligands oxo > imido > alkyl.⁴

Table 2.2: Selected Bond Lengths (Å) and Angles (°) for compound 2.

<u>1</u>	<u>2</u>	<u>3</u>	<u>1-2</u>	<u>1-2-3</u>
O	Mo	N	1.706(2)	103.68(9)
O	Mo	N1		158.69(8)
O	Mo	N2		84.04(8)
O	Mo	N3		101.76(8)
N	Mo	N1	1.760(2)	97.56(8)
N	Mo	N2		168.68(8)
N	Mo	N3		90.07(8)
N	Mo	C10		101.46(9)
N1	Mo	N2	2.379(2)	74.68(6)
N1	Mo	N3		76.13(6)
N1	Mo	C10		80.49(9)
N2	Mo	N3	2.321(2)	80.14(7)
N2	Mo	C10		85.59(8)
N3	Mo	C10	2.207(2)	155.10(8)
C10	Mo	O	2.191(2)	96.89(10)
C20	N	Mo	1.386(3)	168.07(13)
C11	C10	Mo	1.552(3)	125.5(2)

In transition metal-oxo and -imido compounds in which the formal electron count of the metal is less than 18 electrons, triply bonded oxo and imido ligands are the preferred valence bond description by donation of a lone pair of electrons of the ligand to an empty metal d orbital of appropriate π -symmetry. In compound 2, however, the metal has an electron count of 20 if both the oxo and the imido are triply bonded. The crystal structure of 2 shows the oxo and the imido ligands to have bond orders between two and three with metal bond lengths of 1.706(2)Å and 1.760(2)Å, respectively.^{4,17,18} Also, the Mo-N-Ar bond angle, 168.07(13)°, approaches linearity, suggesting to a first approximation that the molybdenum-nitrogen bond order is greater than two. However, the steric bulk at the metal center may also contribute to the linearity of the sterically demanding aryl imido ligand. A delocalized, three center-four electron π -bonding description between the oxygen, molybdenum, and nitrogen atoms may provide the best explanation of the metal's ability to accommodate twenty electrons.

Crystal Structure of $[\text{TpMo}(\text{NAr})(\text{O})]_2\text{O}$ (**3**)

A red single crystal suitable for x-ray diffraction studies was isolated from the pentane mother liquor of **2** after two weeks. The structure of $[\text{TpMo}(\text{NAr})(\text{O})]_2\text{O}$ (**3**), shown in Figure 2.7, was obtained. Compound **3** appears to be a hydrolysis product of compound **2** in which the neophyl ligands of two equivalents of **2** are protonated and lost and the metal centers are bridged by an oxygen atom, most likely from H_2O . The synthesis of compound **3** was attempted in two ways. H_2O and 2,6-lutidine were added to compound **2** dissolved in THF, and H_2O and HBF_4 were added to **2** dissolved in Et_2O . Both attempts were unsuccessful with only unreacted **2** being recovered. $[\text{TpMoOCl}]_2\text{O}$, a molybdenum (V) analogue of **3** has been prepared by the hydrolysis of TpMoCl_3 .⁹¹

The crystal structure of compound **3** shows the molecule to possess a center of inversion at the position of the bridging oxygen atom, with the oxo, imido, and other ligands being *trans* to one another. Selected bond distances and angles are given in Table 2.3. The crystal consists of well-separated molecules with the pseudooctahedral coordination geometry and metal-ligand bond lengths about the molybdenum centers not differing remarkably from that of compound **2**. The N-Mo bond lengths of the chelating pyrazole rings range from 2.342(11) Å to 2.200(12) Å and are consistent with the decreasing *trans* influence of terminal oxo > imido > bridging oxo [1]. The Mo-O1-Mo_a angle is linear as required by symmetry and the Mo-O1 bond length (1.879(1) Å) is shortened⁹² suggesting the bridging oxygen can participate in stabilizing the d^0 metal centers through $d\pi$ - $p\pi$ donation. However, the steric bulk about the molybdenum atoms likely contribute to the linearity of the Mo-O1-Mo_a angle.

It is concluded that the stability of the described molybdenum compounds arises from the chelating ability of the Tp ligand and the presence of coordinatively and electronically saturated metal centers. The Tp ligand provides a template on which the hydrolysis products of the metal alkylidene can be observed and characterized. The molybdenum oxo imido compounds characterized crystallographically in this dissertation

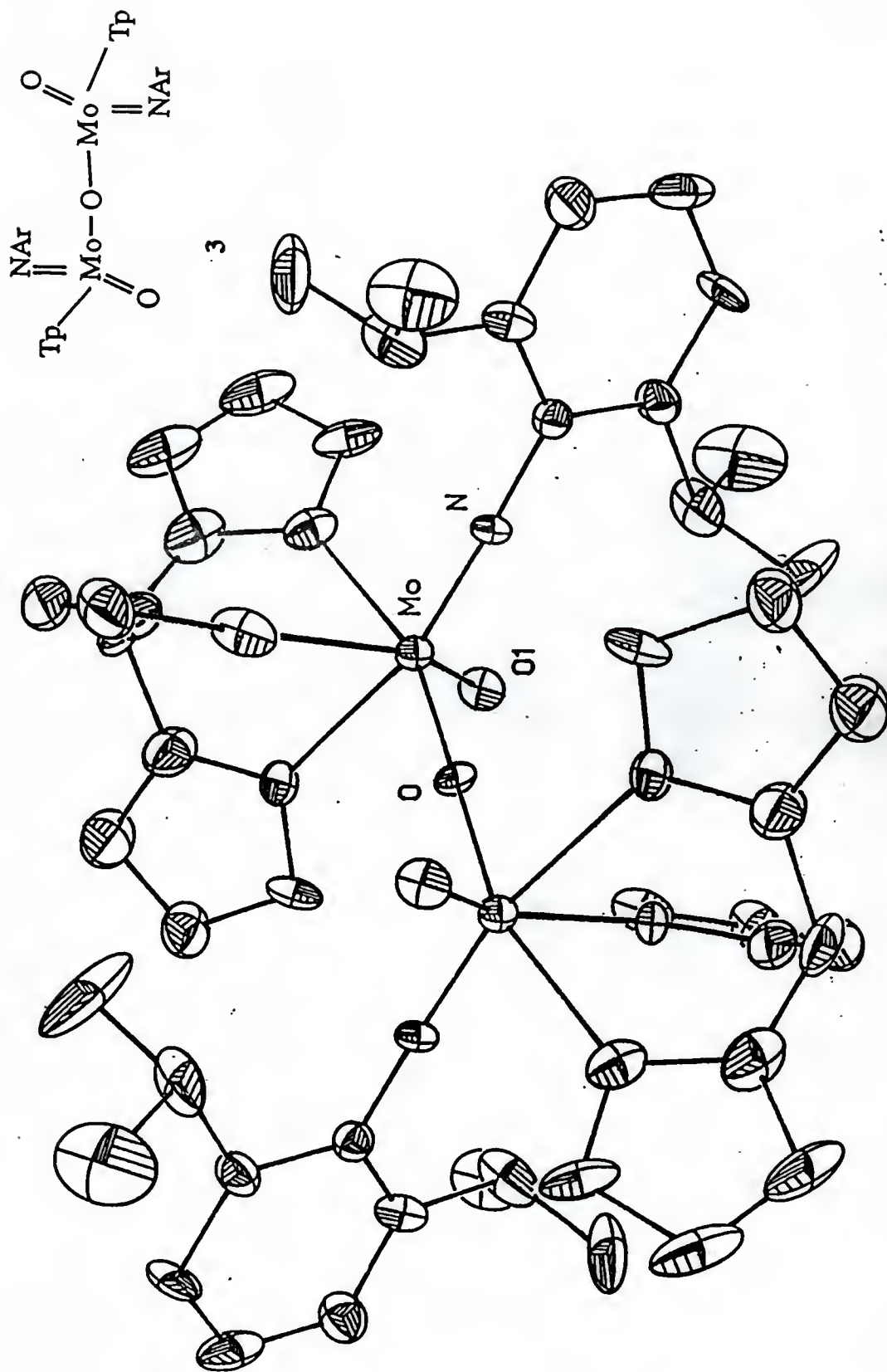


Figure 2.7. Thermal ellipsoid plot of $[\text{TpMo}(\text{NAr})(\text{O})]_2\text{O}$ (3).

demonstrate the effects of competition between the multiply bonded ligands for the limited number of π -symmetry metal orbitals.

Table 2.3: Selected Bond Lengths (Å) and Angles (°) for compound 3.

<u>1</u>	<u>2</u>	<u>3</u>	<u>1-2</u>	<u>1-2-3</u>
N1	Mo	N3	1.728(9)	95.3(4)
N1	Mo	N5		87.9(5)
N1	Mo	N7		165.6(4)
N1	Mo	O1		101.7(3)
N3	Mo	N5	2.342(11)	78.0(4)
N3	Mo	N7		73.6(4)
N3	Mo	O1		82.5(3)
N3	Mo	O2		158.0(4)
N5	Mo	N7	2.200(12)	80.8(4)
N5	Mo	O1		159.0(3)
N5	Mo	O2		92.2(4)
N7	Mo	O1	2.309(11)	86.3(3)
N7	Mo	O2		85.5(4)
O1	Mo	O2	1.8789(12)	103.3(3)
O2	Mo	N1	1.706(8)	104.0(4)
O1	Mo _a		1.8789(12)	
C1	N1	Mo	1.41(2)	168.1(8)
Mo	O1	Mo _a		180.(0)

Synthesis and Characterization of TpMo(CHC(CH₃)₂Ph)(NAr)(OCH₃) (4)

So far, the compounds of the general formula TpM(CHC(CH₃)₂R)(NAr)(X) [M = Mo, W; R = CH₃, C₆H₅; X = Cl, Br, OTf, pyrazolide, alkyl] described herein and elsewhere have X being electron withdrawing substituents and/or poor π donors.^{76-78,83} We were interested in replacing the triflate ligand in compound 1 with a better π donating substituent, namely methoxide, to observe how this substitution would effect the chemistry of these molecules.

Similar to the hydrolysis of 1 to give TpMo(CH₂C(CH₃)₂Ph)(NAr)(O), TpMo(CHC(CH₃)₂Ph)(NAr)(OCH₃) (4, Figure 2.8) was prepared by the methanolysis of 1 stirred in the presence of Florisil. Extraction and recrystallization of 4 afforded yellow

crystals. An unidentified insoluble white powder remained from the pentane extraction, however a low resolution mass spectrum indicated the presence of molybdenum.

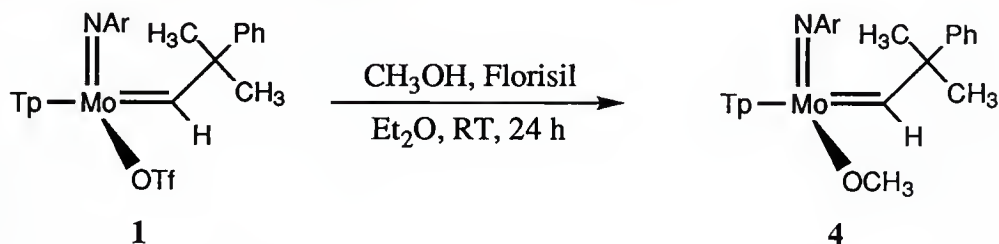


Figure 2.8. Synthesis of $\text{TpMo}(\text{CHC}(\text{Me})_2\text{Ph})(\text{NAr})(\text{OCH}_3)$ (**4**).

The ^1H NMR spectrum (Figure 2.9) of compound **4** at 22 °C is comparable to its parent compound. The spectrum has nine distinct pyrazole proton resonances and diastereotopic methyl groups for the neophylidene ligand and isopropyl groups of the aryl imido ligand. The broadening of the isopropyl group proton resonances suggests hindered rotation about the nitrogen-aryl bond due to the steric demands of the Tp ligand. The chemical shift of the alkylidene proton is δ 13.14. This is one of the highest field shifts for these molybdenum alkylidene compounds indicating a more electron rich metal center. The new resonance corresponding to the methyl protons of the methoxide ligand is found at δ 4.60. Absorptions due to the methoxide ligand are also observed in the IR spectrum at 2778.2 and 1081.8 cm^{-1} corresponding to the methoxy C-H and C-O stretches, respectively.

Synthesis and Characterization of $\text{TpMo}(\text{CC}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{OCH}_3)$ (**5**)

In a separate attempt to prepare $\text{TpMo}(\text{CHC}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{OCH}_3)$, compound **1** was allowed to react with one equivalent of potassium methoxide in THF at room temperature. The solution color changed from yellow to red-orange, and recrystallization of the product from pentane gave orange crystals. A ^1H NMR spectrum (Figure 2.10) of the product showed loss of the alkylidene resonance and the appearance of two broad

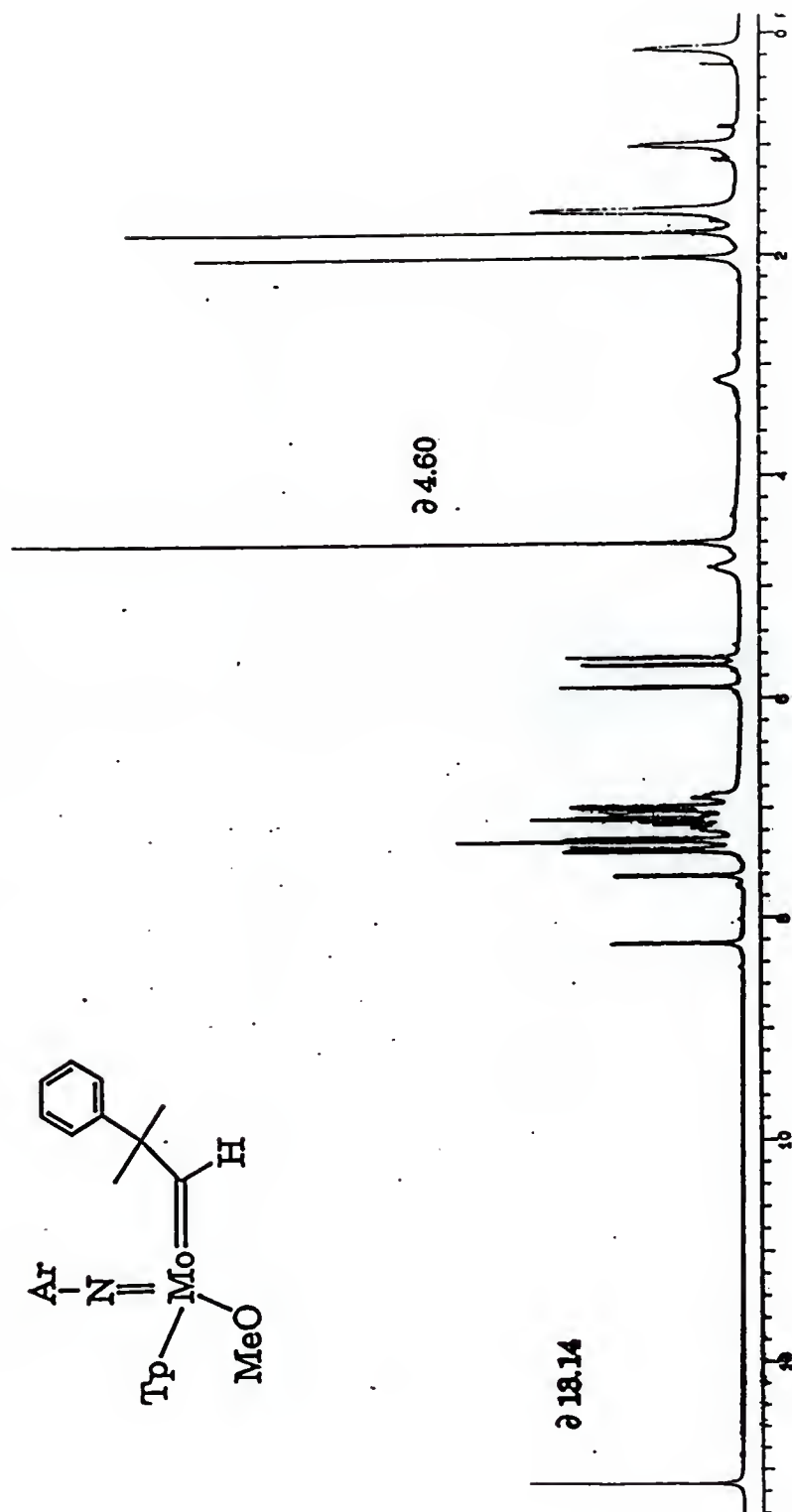


Figure 2.9. ^1H NMR spectrum of $\text{TpMo}(\text{CHO})(\text{CH}(\text{Ph})_2)(\text{NAr})(\text{OMe})$ (4).

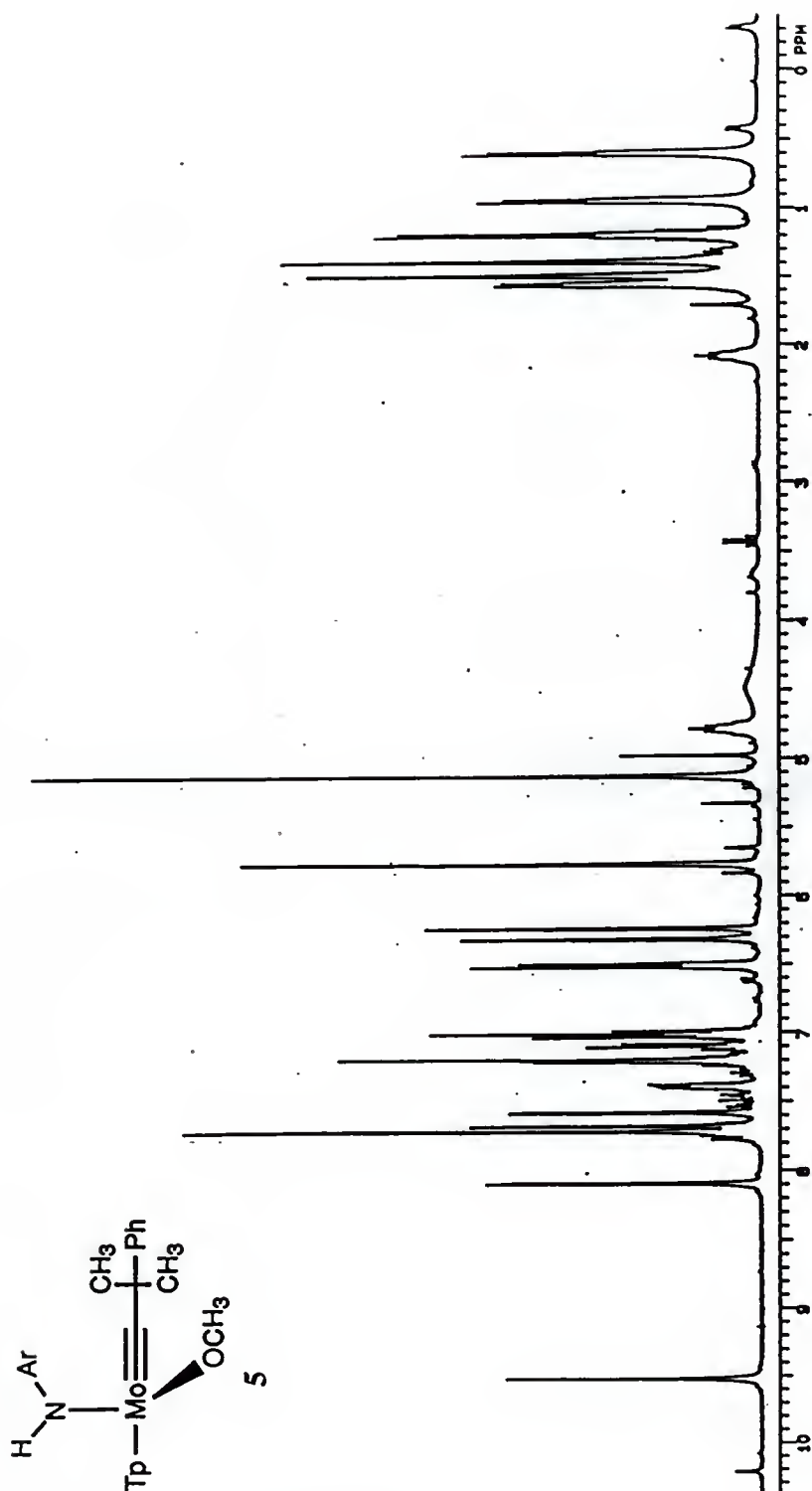


Figure 2.10. ^1H NMR spectrum of $\text{TpMo}(\text{CC}(\text{CH}_3)_2\text{Ph})(\text{NHAr})(\text{OCH}_3)$ (**5**).

singlets at δ 9.55 and δ 10.26 and two methoxide singlets at δ 5.11 and δ 4.98. A ^{13}C {H} NMR spectrum confirmed the presence of sp-hybridized alkylidyne carbons at δ 301.7 and δ 298.7, and the structure was determined to be the major and minor rotamers of $\text{TpMo}(\text{CC}(\text{CH}_3)_2\text{Ph})(\text{NHAr})(\text{OCH}_3)$ (**5**, Figure 2.11). This molybdenum amido alkylidyne complex is the tautomer of **4**.

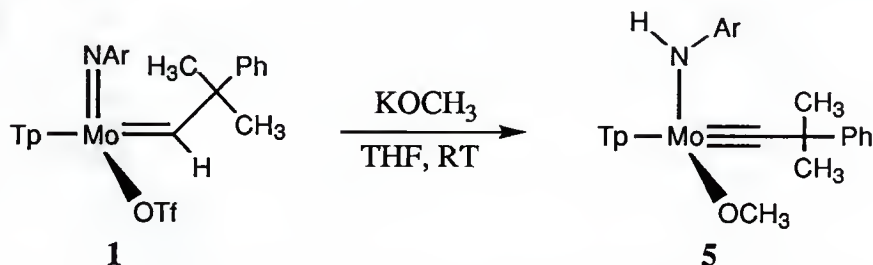


Figure 2.11. Synthesis of $\text{TpMo}(\text{CC}(\text{Me})_2\text{Ph})(\text{NHAr})(\text{OCH}_3)$ (**5**).

The major and minor isomers arise from rotational isomers of the molybdenum-amide bond. Variable temperature ^1H NMR experiments showed the two amide proton resonances to coalesce at 65 °C. This corresponds to an activation energy, $\Delta G^\ddagger$, of 15.7 kcal/mol. Cooling the solution to room temperature reestablishes the same equilibrium ratio of rotamers and shows that ΔG° for the two rotamers is 0.8 kcal/mol. The IR spectrum of **5** reveals a single sharp absorption at 3308.7 cm^{-1} for the N-H stretch of the amido ligand.

Since compounds **4** and **5** are formally related by transfer of the alkylidene proton to the nitrogen of the imido ligand, we tried to convert **4** to **5**. Compound **4** was stable towards tautomerization for one week in dg-toluene. Photolysis, continued heating at 110 °C, and addition of Lewis bases (NEt_3 , $\text{P}(\text{CH}_3)_3$) did not cause tautomerization of **4** to give **5**. Only the addition of excess potassium methoxide caused the proton to transfer from the alkylidene to the imido ligand. To avoid adding excess methoxide, a THF solution of 0.9 equivalents of potassium methoxide was added dropwise to **1**. However, only **5** resulted from this method of addition.

The experimental results concerning the formation of **5** and orbital considerations suggest that the mechanism for the formation of **5** involves a methoxide mediated proton transfer.

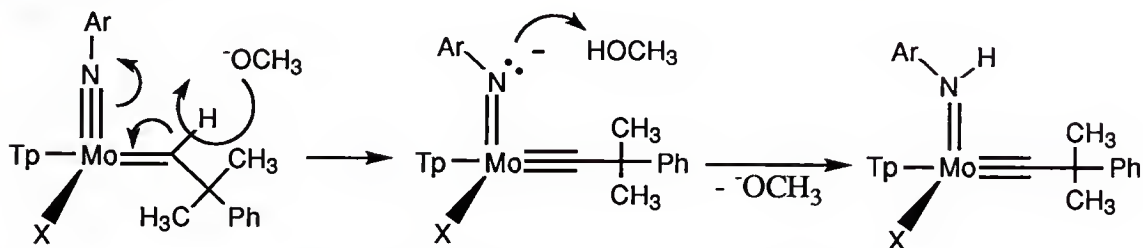


Figure 2.12. Proposed mechanism of the formation of **5**.

In Figure 2.12, a methoxide anion deprotonates the alkylidene ligand of either the starting material, **1**, or compound **4** forming an anionic molybdenum species with the negative charge localized on the imido nitrogen. Following this step is a reprotonation of the metal complex at the nitrogen by methanol. The reverse reaction to deprotonate the amido ligand and reform the alkylidene is less likely due to the stability of the strong metal-carbon triple bond. Also, the amide would be expected to be less acidic in complexes with good π -donors versus those with electron-withdrawing triflates. The conversion of **4** to **5** is the reverse of the proton transfer reaction observed by Schrock and co-workers for the NEt₃-catalyzed conversion of M(NHAr)(C-*t*-Bu)(dme)Cl₂ to M(NAr)(CH-*t*-Bu)(dme)Cl₂ [M = W, Mo]. They observed that the same reaction was impossible when the chlorides of the metal amido alkylidyne complexes were replaced with hexafluoro-*t*-butoxide ligands.^{41,42,93}

Attempts to isolate derivatives of **4** and **5** with the stoichiometry TpMo(CC(CH₃)₂Ph)(NHAr)(X) [X = N(CH₃)₂, O-*p*-tol, OPh] were unsuccessful giving complex mixtures of imido-alkylidene, amido-alkylidyne, and other species which have proven impossible to separate.

Crystal Structure Determination of 4 and 5

The structure of compound **4** was determined by X-ray diffraction methods and a thermal ellipsoid plot is found in Figure 2.13. Selected bond distances and angles are given in Table 2.4. The structure consists of well-separated molecules with the coordination geometry around the molybdenum atom in **4** being a distorted octahedron. The geometric constraints of the facially-bound Tp ligand force the alkylidene, imido, and methoxide ligands to be mutually *cis*. The N-Mo bond lengths of the chelating pyrazole rings range from 2.327(10)Å to 2.232(8)Å and are consistent with the decreasing *trans* influence of the ligands imido > alkylidene > methoxide.¹

Table 2.4: Bond Lengths (Å) and Angles (°) for compound **4**.

<u>1</u>	<u>2</u>	<u>3</u>	<u>1-2</u>	<u>1-2-3</u>
O1	Mo	N1	1.960(7)	100.6(4)
O1	Mo	N2		155.1(4)
O1	Mo	N4		81.7(3)
O1	Mo	N6		84.9(3)
N1	Mo	N2	1.741(9)	99.2(4)
N1	Mo	N4		168.5(4)
N1	Mo	N6		90.9(4)
N1	Mo	C1		102.1(5)
N2	Mo	N4	2.232(8)	76.0(4)
N2	Mo	N6		79.8(3)
N2	Mo	C1		90.5(4)
N4	Mo	N6	2.327(10)	78.0(3)
N4	Mo	C1		88.5(5)
N6	Mo	C1	2.295(8)	165.0(4)
C1	Mo	O1	1.963(10)	100.0(4)
C32	O1	Mo	1.37(2)	130.1(7)
C11	N1	Mo	1.390(14)	169.7(8)
C4	C1	Mo	1.56(2)	136.8(10)

The *cis* orientation of the aryl imido ligand and alkylidene ligand allows for maximum d π -p π bonding between the molybdenum and the multiply bonded ligands. The Mo-N1 bond length of 1.741(9) Å and Mo-N1-C11 bond angle of 169.7(8)° are within

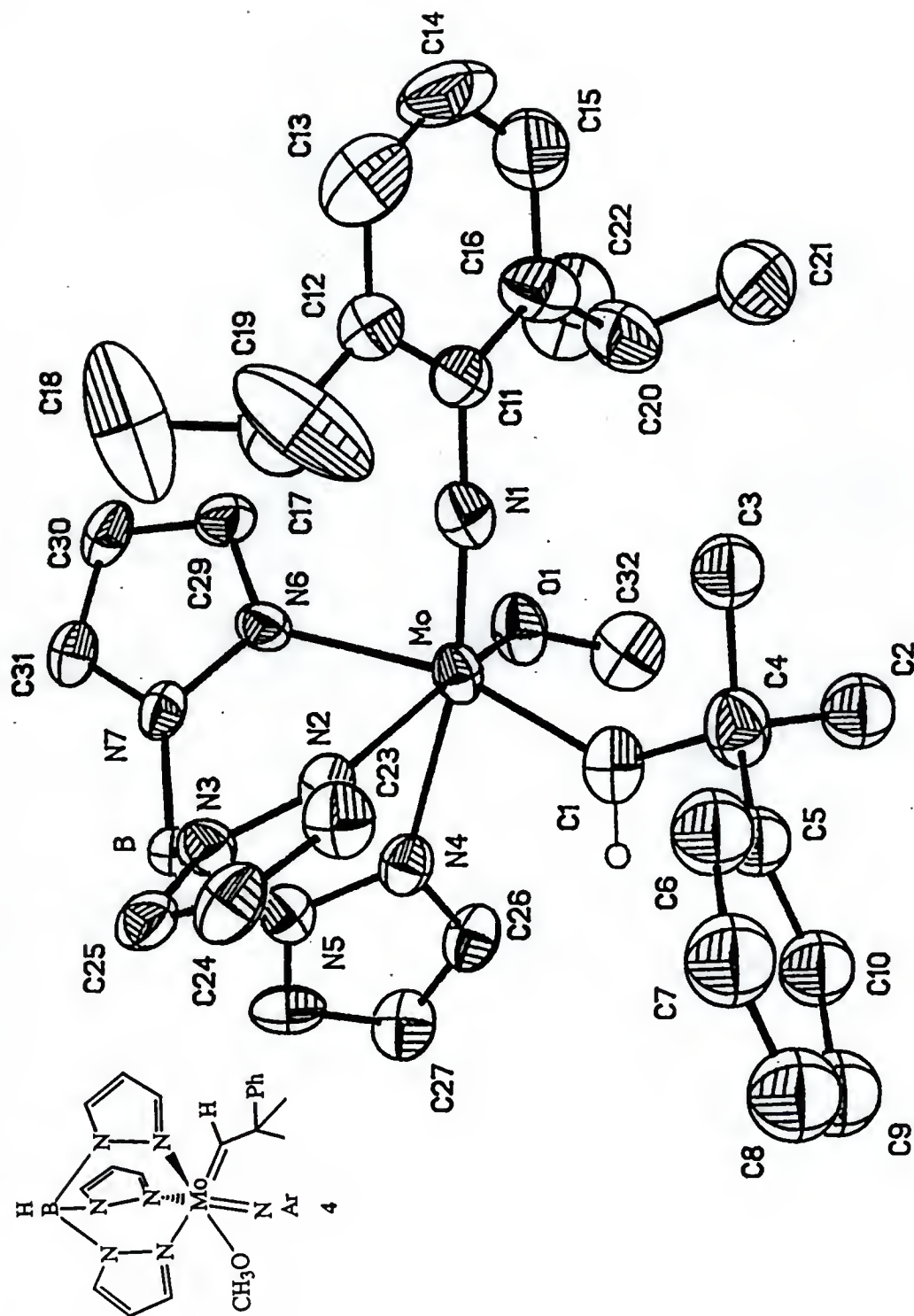


Figure 2.13. Thermal ellipsoid plot of $\text{TpMo}(\text{CHC}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{OCH}_3)$ (4).

normal ranges for molybdenum imido complexes in which the molybdenum-nitrogen bond can be considered to be triply bound with the lone pair of the nitrogen donating to an empty $d\pi$ orbital of the d^0 molybdenum atom. The Mo-C1 bond length, 1.963(10) Å, lies within the expected range for molybdenum-carbon double bonds, and the -C(CH₃)₂Ph group of the alkylidene is in the *syn*, or *s-cis*, orientation with respect to the imido ligand. The steric requirements of the bulky aryl imido group force the Mo-C1-C4 angle to open to 136.8(10) Å. The *syn* orientation is preferred to the *anti* orientation due to the apparently unfavorable steric interaction of wedging the -C(CH₃)₂Ph group between two pyrazole rings of the Tp ligand.

The crystal structure of compound **5** was also determined by X-ray diffraction methods and a thermal ellipsoid plot is found in Figure 2.14. Selected bond distances and angles are given in Table 2.5. Similar to **4**, the geometry around the molybdenum is a distorted octahedron dictated by the geometric and electronic constraints of the Tp ligand. The N-Mo bond lengths of the chelating pyrazole rings range from 2.386(4)Å to 2.235(4)Å and are also consistent with the decreasing *trans* influence of the ligands alkylidyne > amido > methoxide.⁴ The Mo-C1 bond length and angle [1.765(4)Å, 177.2(4)°] are within accepted ranges for d^0 molybdenum alkylidyne bonds, and the sp hybridized alkylidyne carbon donates to two metal d orbitals of π symmetry. Thus, compound **5** is formally a sixteen electron complex with one $d\pi$ metal orbital available for electron donation from the aryl imido and/or methoxide ligands.

The molybdenum-aryl amido bond length and the Mo-N-C angle [1.952(3)Å, 141.1(3)°] differ markedly from the triply bound and linear aryl imido ligand of **4**. The amido proton was located for compound **5**, and the geometry about the amido nitrogen is essentially planar. This planar geometry is consistent with the lone pair of the nitrogen being donated to the empty metal $d\pi$ orbital making compound **5** an eighteen electron complex. Notably, the orientation of the aryl amido ring is that of the *syn* rotamer in the solid state structure with the ring situated towards the alkylidyne ligand, though in solution

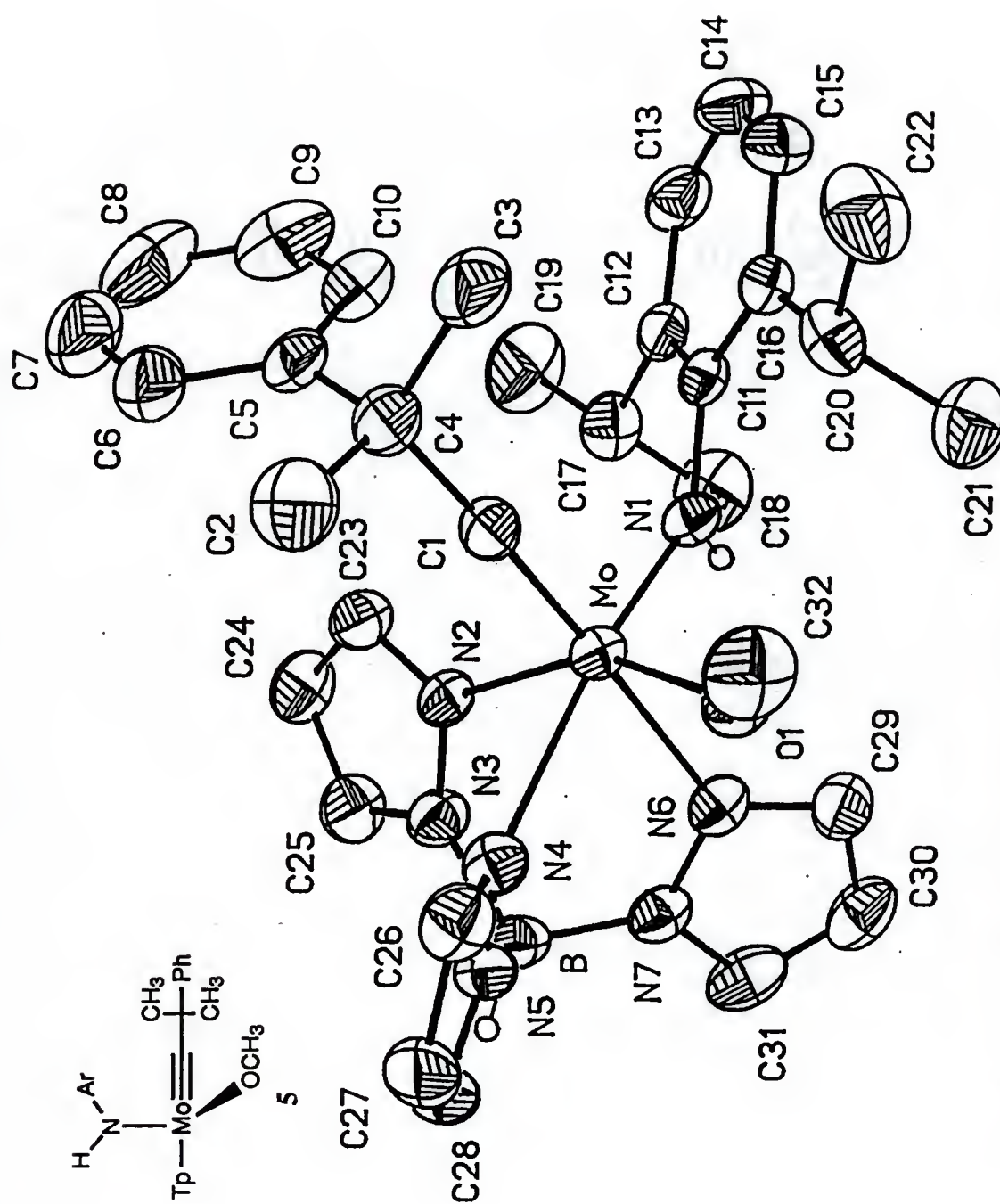


Figure 2.14. Thermal ellipsoid plot of $\text{TpMo}(\text{CC}(\text{CH}_3)_2\text{Ph})(\text{NHAr})(\text{OCH}_3)$ (5).

both rotamers are present. The *syn* rotamer is assumed be the major rotamer in solution. The molybdenum-methoxide bond in compound **5** is slightly shorter than the Mo-O bond of compound **4** by 0.032 Å, and may indicate a higher degree of π -bonding between the oxygen atom in **5** versus **4**. However, as evidenced by the geometry about the nitrogen and the respective *trans* influence of the amido and the methoxide ligands, the amide is a better π donor than the methoxide.

Table 2.5: Selected Bond Lengths (Å) and Angles (°) for compound **5**.

<u>1</u>	<u>2</u>	<u>3</u>	<u>1-2</u>	<u>1-2-3</u>
O1	Mo	N1	1.928(3)	102.9(2)
O1	Mo	N2		155.46(12)
O1	Mo	N4		83.56(14)
O1	Mo	N6		85.36(14)
N1	Mo	N2	1.952(3)	94.2(2)
N1	Mo	N4		160.7(2)
N1	Mo	N6		80.48(14)
N1	Mo	C1		97.6(2)
N2	Mo	N4	2.235(4)	74.87(13)
N2	Mo	N6		80.24(14)
N2	Mo	C1		93.7(2)
N4	Mo	N6	2.265(3)	81.95(12)
N4	Mo	C1		99.0(2)
N6	Mo	C1	2.386(4)	173.5(2)
C1	Mo	O1	1.765(4)	101.2(2)
C32	O1	Mo	1.398(7)	131.7(3)
C11	N1	Mo	1.419(5)	141.1(3)
C4	C1	Mo	1.510(6)	177.2(4)
H1	N1	C11	0.76(4)	109.(3)
H1	N1	Mo		109.(3)

Cationic Molybdenum Imido Alkylidene Complexes

The stability imposed at the molybdenum metal center by the tridentate Tp ligand enables the modification of the TpMo(ChC(CH₃)₂Ph)(NAr) template by varying the ligand in the sixth coordination site. One goal of this research was to prepare cationic molybdenum alkylidenes and to observe how the increased electrophilicity of the metal center modifies the properties of these compounds. The general scheme that was employed

for such a transformation was to abstract an alkyl group from a complex of the type $\text{TpMo}(\text{CHC}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{alkyl})$ in the absence of a coordinating anion to give the desired cationic metal complex. By employing large, non-coordinating counterions, the open coordination site of the cationic complex should readily bind olefin substrates or coordinating solvent molecules. Similar schemes have been successful in preparing and isolating cationic catalysts for olefin-insertion polymerizations.^{94,95} Cationic tungsten alkylidenes have been prepared by using Brønsted acids of non-coordinating anions to protonate the complex followed by loss of the alkyl ligand.⁷⁸

Synthesis and Characterization of $\text{TpMo}(\text{CHC}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{CH}_3)$ (6)

For the purposes of eventually preparing cationic alkylidenes, the alkylation of **1** with a methyl group proved to be the most facile route. The transmetallation of **1** with a moderate excess of methyl lithium in Et_2O at ambient temperature gave $\text{TpMo}(\text{CHC}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{CH}_3)$ (**6**, Figure 2.15) in good yield. Compound **6** exhibits marked air and moisture stability. Compound **6** can be purified over neutral alumina and is stable as a solid in air indefinitely. Stirring **6** in THF with an equivalent of H_2O showed no reaction. In d_8 -toluene at 80°C over 3.5 hours, compound **6** decomposes, forming unidentified products.

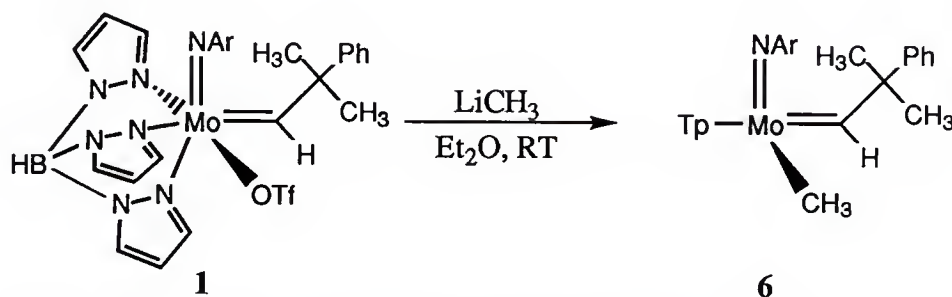


Figure 2.15. Synthesis of $\text{TpMo}(\text{CHC}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{CH}_3)$ (**6**).

The ^1H NMR spectrum (Figure 2.16) of **6** at 22 °C is complicated by the asymmetry of the molecule, resulting in nine distinct pyrazolyl ring proton resonances and diastereotopic neophyl methyl resonances. The alkylidene proton resonance is shifted upfield from that of **1** at 14.73 ppm to 13.11 ppm, and the $^1\text{J}_{\text{CH}}$ observed in the $^{13}\text{C}\{\text{H}\}$ spectrum is reduced slightly to 115 Hz. The methyl proton signal at 1.29 ppm is a sharp singlet, and the methyl carbon resonance at 18.0 ppm in the ^{13}C NMR has a $^1\text{J}_{\text{CH}}$ of 123 Hz. This ^1H - ^{13}C coupling constant is normal for sp^3 C centers⁹⁶ and does not suggest any interaction of the C-H σ bond with the metal center as is expected for a coordinatively and electronically saturated metal complex.⁵ The proton signals for the isopropyl groups of the aryl imido ligand are broadened and occur in a 6:3:3 ratio, suggesting sterically hindered rotation about the carbon-nitrogen bond. Hindered rotation has been observed in other Tp aryl imido alkylidenes.⁷⁷

Protonation of **6** with one equivalent of triflic acid in C_6D_6 resulted in a quantitative conversion to $\text{TpMo}(\text{CHC}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{OTf})$ (**1**) and methane. Addition of a second equivalent of triflic acid causes loss of the alkylidene proton resonance and formation of unidentified decomposition products. In the presence of one equivalent of H_2O , treatment of **6** with triflic acid in Et_2O only yielded **1**.

Synthetic Routes to Cationic Molybdenum Imido Alkylidene Complexes

Removing the methyl group from compound **6** led to several cationic molybdenum alkylidene complexes. Three methods were successfully employed to remove the methyl ligand: protonation by the acid of a non-coordinating anion, abstraction by the trityl cation, and abstraction by a boron-containing Lewis acid. The anions used were fluorinated aryl borates that have been used as non-coordinating anions to stabilize group 4 metallocene cations.^{94,95}

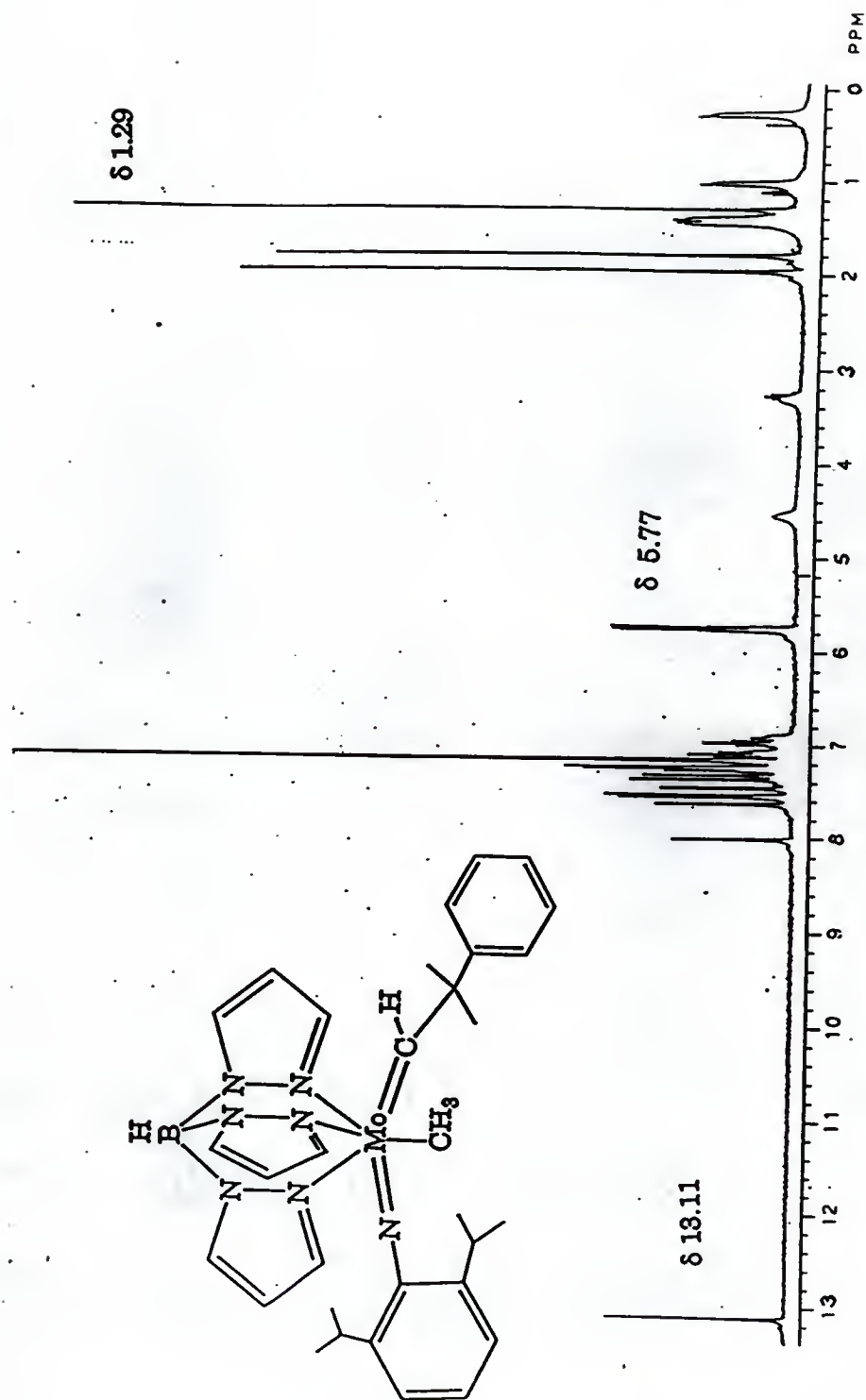


Figure 2.16. ^1H NMR spectrum of $\text{TpMo}(\text{CHO}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{CH}_3)$ (6).

The addition of tetrakis(3,5-trifluoromethylphenyl)boric acid ($\text{HBAr}'_4 \cdot 2 \text{Et}_2\text{O}$, $\text{Ar}' = 3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2$)⁹⁷ to a Et_2O solution of **6** at -78°C gave the thermally unstable cation $[\text{TpMo}(\text{CHC}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{Et}_2\text{O})][\text{BAr}'_4]$ (**7**, Figure 2.17) as a brown oily solid and methane. Compound **7** is insoluble in hydrocarbons and benzene, and the cation decomposes within hours at room temperature in CD_2Cl_2 .

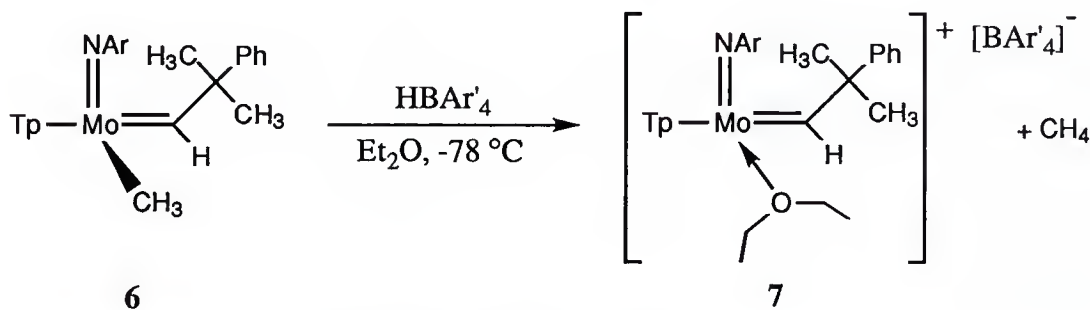


Figure 2.17. Protonation of **6** to give a cationic complex.

The ^1H NMR spectrum (Figure 2.18) of **7** indicates the highly electrophilic nature of this cationic complex. The chemical shift of the alkylidene proton is at δ 14.79, and is shifted significantly downfield from that of compound **6**. A diethyl ether molecule is tightly bound to the metal center as indicated by the ABX_3 coupling pattern for the methylene protons. The ether molecule freely rotates on the NMR time scale interchanging the two sets of diastereotopic methylene protons. At room temperature, four doublets and two septets are observed for the isopropyl groups of the aryl imido ring indicating that the C-N bond of the aryl-imido group does not rotate on the NMR time scale.

Using the trityl cation to abstract the methyl ligand,⁹⁴ the reaction of **6** and trityl tetrakis(pentafluorophenyl)borate in the presence of excess acetonitrile gave $[\text{TpMo}(\text{CHC}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{NCCH}_3)][\text{B}(\text{C}_6\text{F}_5)_4]$ (**8**, Figure 2.19) and Ph_3CCH_3 . The cationic product was obtained as a yellow-brown solid which was insoluble in benzene and saturated hydrocarbons. Efforts to obtain crystals of **8** failed, but precipitation from Et_2O afforded an analytically pure solid.

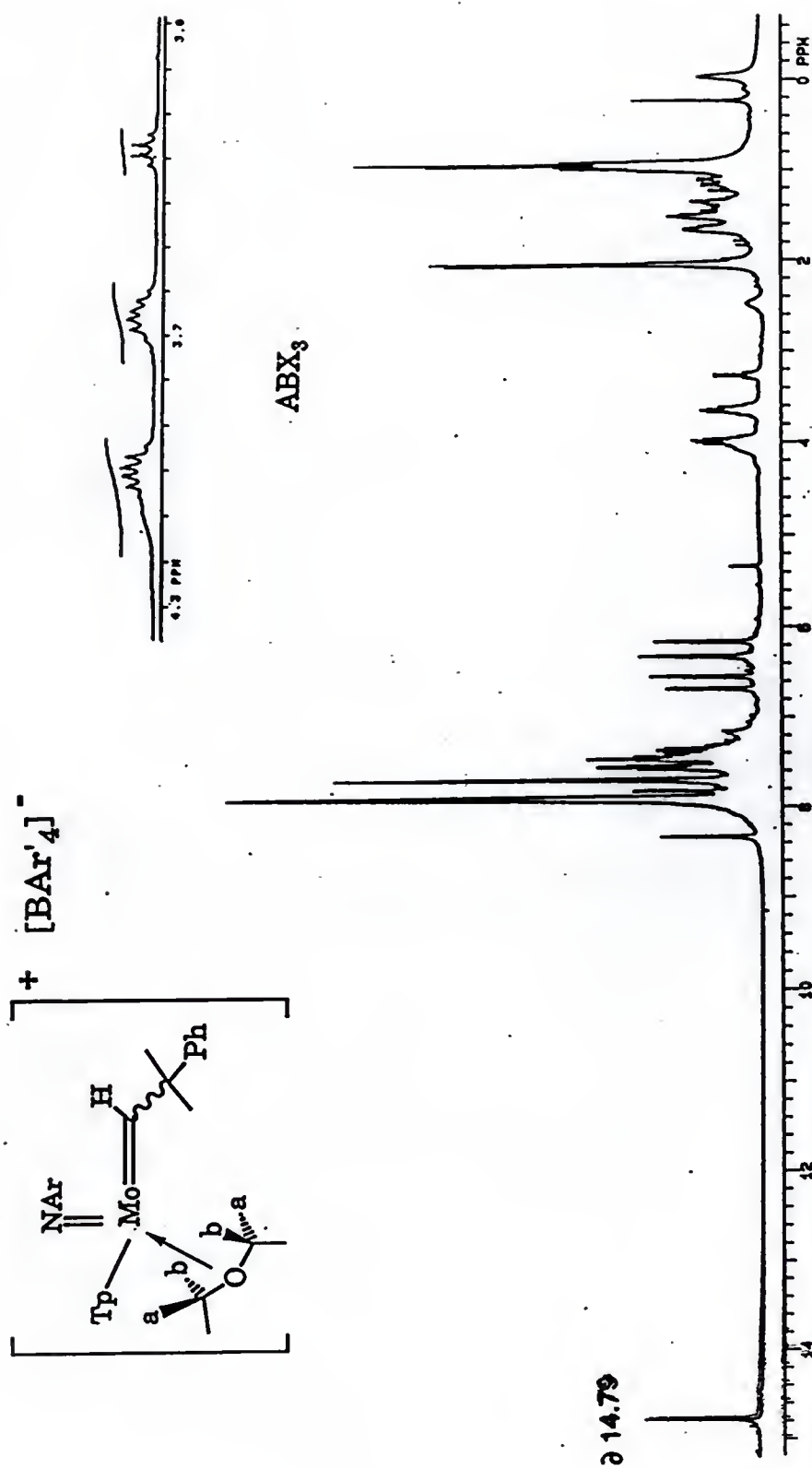


Figure 2.18. ^1H NMR spectrum of $[\text{TpMo}(\text{Chc}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{Et}_2\text{O})][\text{BAR}'_4]$ (7).

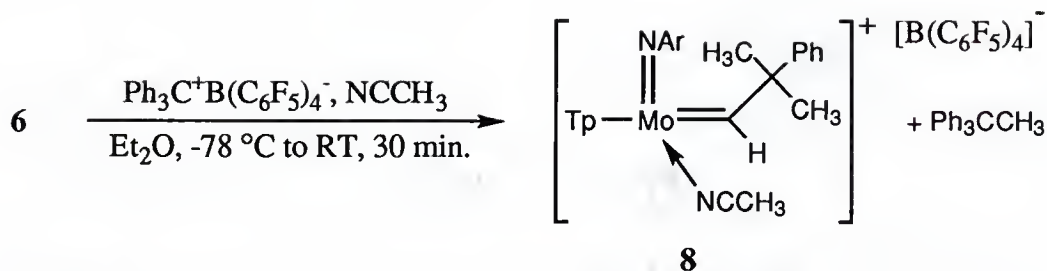


Figure 2.19. Abstraction of the methyl ligand of **6** by the trityl cation to give a cationic complex.

The ^1H NMR spectrum of **8** at $-40.0\text{ }^\circ\text{C}$ shows two distinct alkylidene rotamers in equilibrium which is *ca* 10 % in the minor isomer. The chemical shifts of the alkylidene protons of the major and minor isomers are shifted downfield relative to the neutral complexes and occur at δ 14.47 and 15.28, respectively. The presence of the tetrakis(pentafluorophenyl)borate anion is confirmed by its broad doublets in the ^{13}C NMR spectrum. The ^1H and ^{13}C NMR resonances of the Tp, aryl imido, and alkylidene ligands are similar to those observed in the parent compounds, and the new resonance for the acetonitrile ligand is prominent at 2.35 ppm in the proton spectrum.

The Lewis acid tris(pentafluorophenyl)boron, $\text{B}(\text{C}_6\text{F}_5)_3$, has been shown to abstract alkyl ligands forming cationic metal complexes.⁹⁵ The addition of $\text{B}(\text{C}_6\text{F}_5)_3$ to an Et_2O solution of **6** in the presence of acetonitrile gives the compound $[\text{TpMo}(\text{CHC}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{NCCH}_3)] [\text{B}(\text{CH}_3)(\text{C}_6\text{F}_5)_3]$ (**9**, Figure 2.20) in which the Lewis acid abstracts the methyl ligand to give methyltris(pentafluorophenyl)borate as the non-coordinating anion. The cationic product was obtained as a yellow-brown solid which was insoluble in hydrocarbons. Efforts to obtain crystals of **9** failed, but precipitation from Et_2O afforded an analytically pure solid.

Similar to **8**, compound **9** is a mixture of two rotamers which is composed of *ca* 10 % of the minor rotamer. The alkylidene proton resonances are deshielded with respect to the neutral complexes and occur at δ 14.53 and δ 15.32 for the major and minor rotamers, respectively. The resonance of the methyl protons of the borate anion is a broad singlet at

0.47 ppm. The remaining NMR spectral data for **9** are similar to those data for **8**. This is not surprising since the only difference between **8** and **9** is the substitution of a methyl group for a perfluorophenyl group on the borate anion.

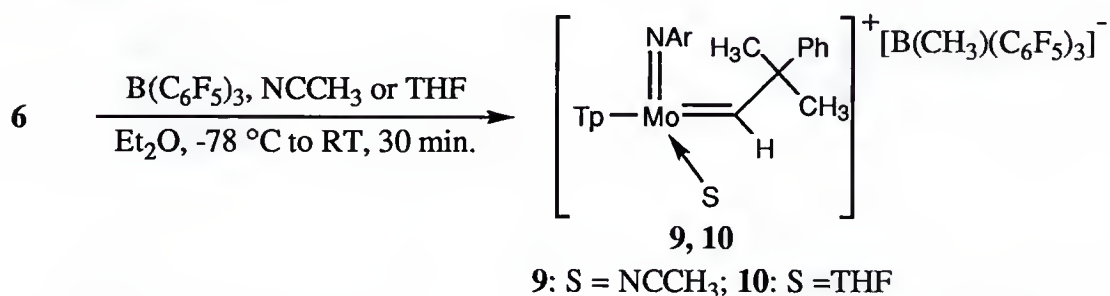


Figure 2.20. Abstraction of the methyl ligand of **6** by the Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ to give a cationic complex.

The THF-coordinated analogue of **9**, [TpMo(ChC(CH₃)₂Ph)(NAr)(THF)] [B(CH₃)(C₆F₅)₃] (**10**, Figure 2.20), was also prepared and isolated as was compound **9**. NMR spectral data of **10** are similar to those of **9**, and the coordinated THF ligand is observed to be rotating slowly on the NMR time scale showing two sets of diastereotopic methylene proton triplets at δ 3.65 and 3.55.

We later found that a cationic complex, [TpMo(ChC(CH₃)₂Ph)(NAr)(P(CH₃)₃)](OTf) (**11**, Figure 2.21), could be prepared directly from compound **1** in quantitative yield by the addition of trimethylphosphine at room temperature. Compound **11** is isolated as a pale yellow powder, and it is soluble in methylene chloride and insoluble in pentane and benzene.

The ^1H NMR spectrum of **11** in CD_2Cl_2 at $-20\text{ }^\circ\text{C}$ is comparable to its parent compound **1** and the other cationic complexes **7-10**. The distinctive feature of the ^1H NMR spectrum of **11** is the $^3J_{\text{PH}}$ coupling to the bound phosphine observed for the alkylidene protons of the two rotamers. The chemical shifts for the alkylidene proton for the major rotamer (δ 14.51, 5.4 Hz, 84%) and the minor rotamer (δ 14.73, 6.2 Hz, 16%) are shifted slightly downfield from that of **1** (δ 14.44). The ^{13}C resonance for the alkylidene a carbon of the major rotamer is also a doublet (δ 335.9, $^2J_{\text{PC}} = 17.6$ Hz). The

^{31}P NMR signals for the coordinated phosphine ligand are observed at -2.83 and -7.81 ppm for the major and minor rotamers, respectively. The ^{19}F signal for the ionic triflate (δ -78.8, vs. CFCl_3) is slightly upfield from the signal for the covalently-bound triflate ligand of **1** (δ -77.7, vs. CFCl_3).⁹⁸ Evidence for an ionic triflate species in **11** is best seen by a comparison of its vibrational spectrum with that of **1**.⁹⁰ The S=O stretching frequency of the free triflate anion of **11** (1268 cm^{-1}) is split into two observable stretching modes in **1** ($1332, 1202\text{ cm}^{-1}$). Also, a S=O stretch at 1048 cm^{-1} for **11** is shifted to 1011 cm^{-1} for **1**.⁹⁹

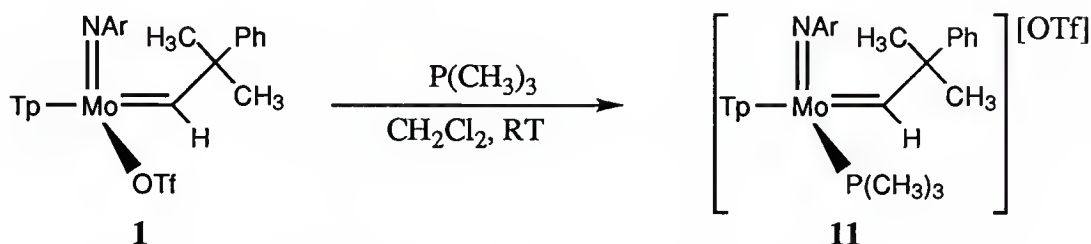


Figure 2.21. Synthesis of $[\text{TpMo}(\text{CHC}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{P}(\text{CH}_3)_3)][\text{OTf}]$ (**11**).

Obviously, the ability of the triflate ligand of **1** to be displaced by trimethylphosphine suggests that the triflate ligand is not as tightly bound as originally considered, and possibly an equilibrium exists between the bound triflate complex (**1**) and a base-free, ionic triflate complex. Such an equilibrium would lie markedly towards the coordinatively and electronically saturated complex **1**, but in the presence of the strongly coordinating phosphine ligand, the base-free cationic complex is consumed to give **11**. Attempts to observe adducts analogous to **11** in CD_2Cl_2 by ^1H NMR by mixing **1** with 30 equivalents of ethylene or 50 equivalents of phenylacetylene were unsuccessful showing only unreacted **1**.

The *Trans* Influence of Ligands in Tp Molybdenum Complexes

The structural data from X-ray diffraction studies for compounds **1-5** provide the opportunity to rank the *trans* influence of a number of ligands. The *trans* influence of a

ligand is its ability to weaken metal-ligand bonds *trans* to it by competition for metal σ and π bonding orbitals. The most direct method to observing the *trans* influence is by observing metal-ligand bond distances.¹⁰⁰ Variation in the molybdenum-pyrazolyl bond distances of compounds **1-5** is used to rank the *trans* influence of the ligands. Thus, the longer the molybdenum-pyrazolyl bond distances correspond to ligands possessing greater *trans* influence. Table 2.6 lists the molybdenum-pyrazolyl bond distances for pyrazolyl rings *trans* to a number of ligands.

Table 2.6. *Trans* influence of ligands in Tp molybdenum complexes.

<i>Trans</i> substituent	Mo-pyrazolyl bond length, Å	Compound
Alkylidyne, CPh(CH ₃) ₂ ³⁻	2.386	5
Oxo, O ²⁻	2.379(2)	2
Imido, NAr ²⁻	2.327, 2.311	1, 2
Alkylidene, CHCPh(CH ₃) ₂ ²⁻	2.311, 2.295	1, 4
Amido, NHA ⁻¹	2.265	5
Alkoxide, OCH ₃ ⁻¹	2.235, 2.232	4, 5
Alkyl, CH ₂ CPh(CH ₃) ₂ ¹⁻	2.207(2)	2
μ -Oxo, Mo-O-Mo, -1	2.200	3
Triflate, OSO ₂ CF ₃ ⁻¹	2.167	1

This table suggests a *trans* influence series of alkylidyne $\approx$ oxo > imido $\approx$ alkylidene > amido > alkoxo > alkyl $\approx$ μ -oxo > triflate. The trends in this series agree with other series in that ligands of higher charge and π -donating abilities have greater *trans* influence.^{4,5,100}

Rotational Isomerism of the Molybdenum-Alkylidene Bond

Rotational isomers are observed for many of the compounds reported in this dissertation. These isomers arise from restricted rotation about the molybdenum-alkylidene double bond and result in *syn* and *anti* rotamers with the neophyl group oriented towards and away from the imido ligand, respectively. Rotational studies for other metal-alkylidene complexes have also been reported in the literature, and electronic effects and orbital

considerations best describe the energetic differences between the related *syn* and *anti* rotamers.^{14,34,36,37} Interestingly, it has been reported that the different alkylidene orientations of $\text{Mo}(\text{CHC}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{OC}(\text{CH}_3)(\text{CF}_3)_2)_2$ can have profound effects on the rates of olefin metathesis.^{34,36} Due to the unique stabilizing ability of the Tp ligand versus the more active alkylidene complexes reported, extensive kinetic studies have been possible for a number of tungsten alkylidene complexes.³⁵ Here we report preliminary studies and evidence for rotational isomerism in several Tp molybdenum alkylidenes.

Irradiating $\text{TpMo}(\text{CHC}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{OTf})$ (**1**) with a sun lamp at $-50\text{ }^\circ\text{C}$ for one hour generated a minor rotamer in a 1:4 ratio with the major rotamer. The alkylidene proton signal for this minor rotamer was observed at δ 14.82, which is 0.09 ppm downfield from the major rotamer. The $^1\text{J}_{\text{CH}}$ of the minor rotamer is 126 Hz compared to 120 Hz for the major rotamer. Large coupling constants (145-155 Hz) have been observed for the *anti* rotamers of four-coordinate alkylidene complexes, and differences in $^1\text{J}_{\text{CH}}$ values have been used to assign *syn/anti* orientations.^{34,36} The electronically and coordinatively saturated nature of **1** minimizes interaction of the alkylidene C-H bond with the metal center that would give rise to large differences in coupling constants for the two rotamers. The major rotamer was determined to be the *syn* rotamer by ^1H nOe difference spectroscopy. The rates of thermal conversion of the *anti* rotamer to the *syn* rotamer were measured from $+40.0\text{ }^\circ\text{C}$ to $+60.0\text{ }^\circ\text{C}$. The activation parameters for this unimolecular process were determined to be $\Delta H^\ddagger = +21.5 \pm 0.3\text{ kcal/mol}$ and $\Delta S^\ddagger = -8.9 \pm 0.8\text{ e.u.}$ The reduction of entropy in the transition state is consistent with restriction of ancillary bond rotation during alkylidene rotation.

For $\text{TpMo}(\text{CHC}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{CH}_3)$ (**6**), only one rotamer is observed at room temperature. Irradiation of **6** in *dg*-toluene by a sun lamp at $-50\text{ }^\circ\text{C}$ generated a new rotamer observed in the low temperature ^1H NMR spectrum at δ 13.78, downfield from the major rotamer at δ 13.04. The rate of thermal conversion of the minor rotamer to the major

rotamer is $3.7 \times 10^{-4} \text{ sec}^{-1}$ at -20.0°C . Similar rates were found for **1** at higher temperatures of $+40.0$ and $+50.0^\circ \text{C}$.

The cationic molybdenum alkylidene complexes, compounds **8**, **9**, **10** and **11**, each have two rotamers present at equilibrium at ambient temperatures. The irradiation of $\text{TpMo}(\text{CHC}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{NCCH}_3)[\text{B}(\text{C}_6\text{F}_5)_4]$ (**8**) by sun lamp at -40°C increased the population of the minor rotamer to 32 % enabling ^1H NMR peak assignments for both isomers. The most notable difference between the spectra of the two rotamers is the 0.8 ppm downfield shift for the alkylidene proton resonance of the minor rotamer versus that of the major rotamer. The rotamer distribution of **8** returned to equilibrium over time upon warming the sample. Irradiation of compounds **7**, **9**, **10** and **11** was not performed.

Rotamers for $\text{TpMo}(\text{CHC}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{OCH}_3)$ (**4**) were not observed at room temperature. Photolysis at -50°C for 90 minutes in dg-toluene using a sun lamp generated a minor rotamer (δ 13.44, 12.5%) which isomerizes thermally to the major rotamer very rapidly. The rate of thermal conversion of the minor rotamer to the major rotamer was measured at -40.0°C with a $k = 3.7 \times 10^{-4} \text{ sec}^{-1}$. From the crystal structure of **4** discussed above, the major rotamer in solution is reasoned to be the *syn* rotamer. This rate compares with the *anti* to *syn* thermal isomerization rate of compound **1** at $+40.0^\circ \text{C}$ where $k = 8.2 \times 10^{-5} \text{ sec}^{-1}$. The extremely fast rates of the alkylidene rotation of **4** made repeated rate measurements at low temperatures difficult, and thus activation parameters were not determined for the compound.

The marked difference in the rates of alkylidene rotation for compounds **1**, **4**, and **6** is best understood by considering the competition for the empty $d\pi$ orbitals of molybdenum by the $p\pi$ orbitals of the alkylidene, imido, and X, where X is a triflate, methyl, or methoxide ligand, respectively. In the ground state, the alkylidene carbon p_y orbital interacts with the metal d_{xy} orbital, and the p_x and p_y orbitals of the imido interact with the metal d_{xz} and d_{yz} orbitals, respectively. In the transition state, where the alkylidene ligand is rotated 90° , the carbon $p\pi$ orbital is of the appropriate symmetry to compete with imido

p_x orbital for the metal d_{xz} orbital. Rehybridization of the nitrogen atom allows the filled alkylidene $p\pi$ orbital to fully donate to the empty d_{xz} orbital, thus lowering the barrier to the transition state. Such a scheme has been proposed and supported by *ab initio* calculations for four-coordinate tungsten and molybdenum imido alkylidenes.^{14,37}

The Tp ligand system employed in compounds **1**, **4**, and **6** force the alkylidene, imido and X ligands to be oriented mutually *cis*. For ligands X with π -donor capabilities, the bonding situation described above is further complicated. Considering **4**, when X is a π -donating methoxide, a $p\pi$ orbital of oxygen can interact with either the d_{yz} or the d_{xy} orbitals, but not the d_{xz} orbital.

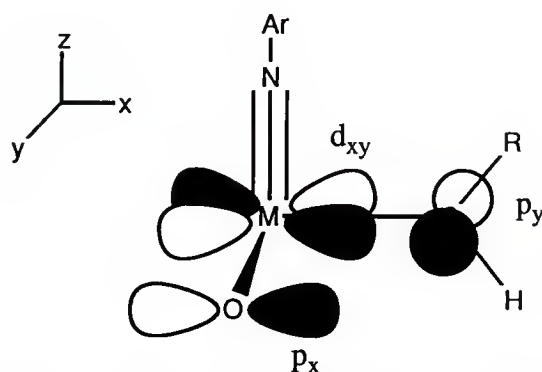


Figure 2.22. Orbital diagram showing competitive donation in the ground state to the metal d_{xy} orbital by the alkylidene and methoxide π electrons.

Interaction of the oxygen p_z orbital with the d_{yz} orbital competes only with a metal-imido π -bond, a bond that is unaffected during alkylidene rotation. Shown in Figure 2.22, interaction of the oxygen p_x orbital with the d_{xy} orbital competes directly with the metal-alkylidene π -bond in the ground state. Such an interaction should raise the ground state energy of the metal-alkylidene bond, resulting in a decrease in the barrier for alkylidene rotation. The kinetic data for alkylidene rotation in **4** versus **1** and **6** support this argument. A similar explanation was offered to describe changes in activation barriers for alkylidene rotation due to changes in the ancillary ligands for d^0 , five-coordinate $W(CHR)(OCH_2-t-Bu)_nX_{4-n}$ complexes.¹⁰¹ Other reports regarding alkylidene rotation

rates for molybdenum aryl imido neopentylidenes also show increased rotational rates as alkoxide substituents become more electron donating, as in the series $\text{OR} = \text{OC}(\text{CH}_3)_3 > \text{OC}(\text{CH}_3)_2(\text{CF}_3) > \text{OC}(\text{CH}_3)(\text{CF}_3)_2 > \text{OC}(\text{CF}_3)_2(\text{CF}_2\text{CF}_2\text{CF}_3)$.^{34,36} Such a relationship is consistent with our finding for the relative rates of rotation for the series, $\text{X} = \text{OCH}_3 > \text{CH}_3 > \text{OSO}_2\text{CF}_3$.

Polymerization Studies

The olefin metathesis activity of these Tp molybdenum complexes was of particular interest considering their thermal stability. However, their electronically and coordinatively saturated nature that imparts the thermal stability also negates their interaction with olefinic substrates, and cocatalysts are required. The metathesis activity of Tp molybdenum alkylidene complexes is detailed below.

Compound **1** is inert toward the metathesis of neat cyclooctene or 1,9-decadiene, and no polymerization was observed for **1** and 500 equivalents of norbornylene in *o*-dichlorobenzene at 80 °C. However, in the presence of the Lewis acid AlCl_3 , **1** quantitatively catalyzed the ring-opening metathesis polymerization of cyclooctene. With a 1:6:500 mixture of **1**, AlCl_3 , and neat cyclooctene, polyoctenamer ($M_n = 57,000$, $M_w/M_n = 1.30$) was formed. This result compares with the tungsten analogue of **1** which quantitatively polymerizes cyclooctene in the presence of a Lewis acid.⁷⁷

A mixture of **1**, AlCl_3 , and 1,9-decadiene at 90 °C under static vacuum only dimerized a small fraction of the monomer to give a degree of polymerization of 2.3 before the catalyst became inactive. The stepwise fashion of ADMET condensation polymerizations require quantitative conversion (> 99 %) of end groups to achieve high polymer. The tungsten analogue of **1** shows very little conversion of 1,9-decadiene to dimer. This result that molybdenum is more active than tungsten for the metathesis of terminal olefins agrees with other reports.^{42,68,83,93}

Compound **6** in the presence of AlCl_3 polymerized norbornylene to give a quantitative yield of poly(norbornylene) in toluene at room temperature. With a 1:7:500 mixture of **6**, AlCl_3 , and neat norbornylene, poly(norbornylene), $M_n = 75,000$ and $M_w/M_n = 1.8$, was formed. A related compound, $\text{TpW}(\text{CHC}(\text{CH}_3)_3)(\text{NAr})(\text{CH}_2\text{C}(\text{CH}_3)_3)$, also catalyzes the ROMP of cyclooctene under similar conditions.⁷⁸

As with **1**, compound **6** and AlCl_3 did not successfully polymerize 1,9-decadiene via ADMET. With a 1:5:500 mixture of **6**, AlCl_3 , and neat 1,9-decadiene, only 7 % of the monomer was converted to dimer during 8 hours of stirring under static vacuum.

Attempts to trap and isolate any unsaturated metal complex from the catalytic mixture of **1** or **6** and AlCl_3 with $\text{P}(\text{CH}_3)_3$ were unsuccessful. Observation of **1** or **6** with AlCl_3 in C_6D_6 by ^1H NMR initially gave a complex mixture, and after several days free pyrazole was observed.

Lewis acids are proposed to play a role in generating a four-coordinate cationic active catalyst in $\text{W}(\text{CHR})(\text{OCH}_2\text{R})_2\text{X}_2/\text{Al}_2\text{X}_6$ metathesis systems.¹⁰²⁻¹⁰⁴ Also, $\text{W}(\text{O})(\text{CHC}(\text{CH}_3)_3)(\text{PEt}_3)_2\text{Cl}_2/\text{AlCl}_3$ metathesizes olefins while the five-coordinate, neutral complex $\text{W}(\text{O})(\text{CHC}(\text{CH}_3)_3)(\text{PEt}_3)\text{Cl}_2$ is an active catalyst in the absence of a Lewis acid.⁶² Contrary to a mechanism involving the Lewis acid simply removing the triflate or methyl ligand of **1** or **6** to generate a five-coordinate, cationic active catalyst, no metathesis activity is seen for the solvent-bound, cationic complexes, **7** and **8**. Contributing to the inactivity of the cationic complexes, the high electrophilicity of the metal center does not allow dissociation of the bound solvent molecule to open a coordination site on these electronically and coordinatively saturated compounds. Heating a CD_2Cl_2 solution of **8** pressurized with ethylene at 60 °C for 24 hours showed no reaction or loss of acetonitrile.

Though five-coordinate metathesis catalysts are known,^{62,102,103} other reported five-coordinate complexes have coordinated bases that are most likely lost to give four-coordinate, active catalytic species.^{79,105} It is proposed that though the role of the Lewis acid may include abstraction of a triflate or methyl ligand to give a five-coordinate, cationic

complex, the Lewis acid also reacts with the Tp ligand system and removes a pyrazole ring from the coordination sphere of molybdenum. This would result in a four-coordinate, 14-electron, cationic complex in which the Tp ligand is bound to the metal center by only two pyrazolyl rings.

Indirect evidence for this proposal is the production of free pyrazole from **1** and **6** in the presence of AlCl_3 mentioned above and the observation that $[\text{TpMo}(\text{CHC}(\text{CH}_3)_2\text{Ph})(\text{NAr})(\text{THF})][\text{B}(\text{CH}_3)(\text{C}_6\text{F}_5)_3]$ (**10**) and two equivalents of AlCl_3 in toluene quantitatively polymerizes 500 equivalents of norbornylene. Further indirect evidence includes the observation that the closely related complex $[\text{TpW}(\text{NPh})(\text{CHCMe}_3)(i\text{-Pr}_2\text{O})][\text{BAR}'_4]$ does not initiate the polymerization of norbornylene even though the diisopropyl ether ligand readily dissociates and is displaced by other Lewis bases such as diethyl ether and acetonitrile.⁷⁸

Conclusion

Undoubtedly, the chelating hydridotris(pyrazolyl)borate ligand plays an important role in the synthesis of air, moisture, and thermally stable molybdenum alkylidene complexes. Since the Tp ligand saturates the complexes both electronically and coordinatively, the metal centers are extremely robust, however they are unreactive towards nonpolar molecules, namely olefins. Though the complexes prepared and characterized in this chapter are not metathesis catalysts in the absence of Lewis acids, insight has been gained as to strategies for developing chelated olefin metathesis catalysts. Therefore, chelating ligands must be chosen such that the complexes are electronically and coordinatively unsaturated under the conditions of catalysis.

CHAPTER 3

THE KINETICS AND MECHANISMS OF REACTIONS INVOLVING PHENYLENEDIAMIDO TUNGSTEN COMPLEXES

Recently our research group has realized the utility of using phenylenediamido ligands to stabilize tungsten complexes. The most extensive work has been with N, N'-bis(trimethylsilyl)-*o*-phenylenediamide (TMS₂pda) which serves as a bidentate, dianionic ligand. VanderLende has synthesized a large variety of alkyl, alkylidene, and hydride complexes starting with (TMS₂pda)W(NPh)(Cl)₂ (**12**).^{79,84} The tungsten alkylidene complex, (TMS₂pda)W(NPh)(CHC(CH₃)₃)(P(CH₃)₃), is thermally stable at 110 °C and successfully polymerizes norbornylene *via* a ring-opening metathesis polymerization mechanism.⁷⁹ These complexes do lack the air and moisture stabilities observed in the Tp complexes of Chapter Two, and in the presence of trace protic species, N, N'-bis(trimethylsilyl)-*o*-phenylenediamine (TMS₂pdaH₂) is observed. This is not unexpected considering the polar nature of tungsten-nitrogen single bonds and the sensitivity of the silicon-nitrogen bond to hydrolysis.

Vanderlende reported the synthesis of both the alkylidene complex and a metallacycle species from the bisalkyl complex (TMS₂pda)W(NPh)(CH₂C(CH₃)₃)₂ (**13**, Figure 3.1).⁸⁴ The thermolysis of **13** at 70 °C in the presence of 5 equivalents of trimethylphosphine gave the α -abstraction product (TMS₂pda)W(NPh)(CHC(CH₃)₃)(P(CH₃)₃) (**14**) in a 66% yield. The thermolysis of **13** in the absence of trimethylphosphine gave a metallacycle complex. This complex was not able to be isolated and was only observed by NMR spectroscopy. Originally, the spectral data was assigned to (TMS₂pda)W(NPh)(CH₂C(CH₃)₂CH₂) (**15**) which would formally result from a γ -abstraction process from **13**. Subsequent investigations by this author

(*vide infra*) revealed the structure of the metallacycle to be a tungstasilacycle (**16**) which might result from γ -CH-activation of a trimethylsilyl group of the ligand by either complex **13** or **14**.

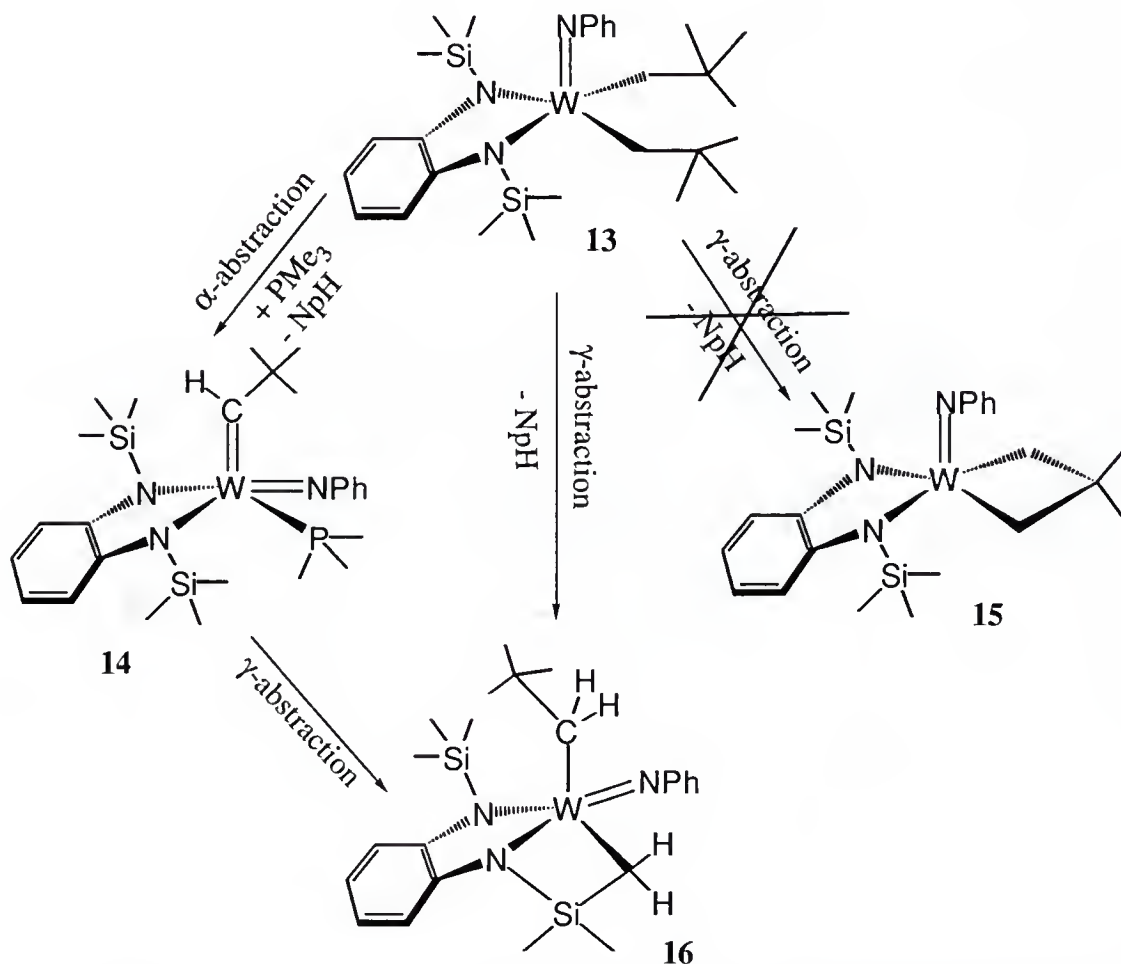


Figure 3.1. Products of the Thermolysis of $(\text{TMS}_2\text{pda})\text{W}(\text{NPh})(\text{CH}_2\text{C}(\text{CH}_3)_3)_2$.

In order to study the formation of **14** and **16**, a number of kinetic and mechanistic experiments have been performed. These experiments include kinetic measurements followed by ^1H NMR spectroscopy and deuterium labeling studies analyzed by mass spectrometry and ^2H NMR spectroscopy. This chapter details the experimental results obtained to date and the mechanistic schemes that are proposed in light of these

investigations. This research is ongoing, and when appropriate, experiments will be suggested that should illuminate facets of our proposed mechanism that are still ambiguous.

Synthesis, Characterization and Structure of the Metallacycle Complex

VanderLende reported the formation of a metallacycle complex from the thermolysis of **13** in toluene at 70 °C for two days.⁸⁴ The assignment of structure **15** to this data was based upon two geminal proton doublets at 2.49 and -1.15 ppm in the ¹H NMR. However, these two doublets were not coupled to one another, as evidenced by selectively irradiating one doublet and observing no perturbation in the resonance of the other doublet. A COSY experiment unequivocally identified two additional doublets which were obscured by the neopentane by-product and unidentified decomposition product resonances (Figure 3.2). The doublet at δ 2.49 is coupled to a doublet at δ 0.76; the doublet at δ -1.15 is coupled to a doublet at δ 0.86. This revelation and other observations to be described later suggested that complex **16** is formed upon thermolysis.

The ¹H NMR spectrum of **16** (Figure 3.3) consists of the aforementioned sets of geminal doublets. The doublets at 2.49 and 0.76 ppm are attributed to the α-methylene protons of the neopentyl ligand, and the doublets at 0.86 and -1.15 ppm are assigned to the α-methylene carbon of the silacycle. Two singlets at 0.54 and 0.20 ppm integrate to three protons each and are assigned to the β and β' methyl groups on the ring silicon. Intense singlets at 1.02 and 0.38 ppm are assigned to the *t*-butyl group of the neopentyl ligand and the free trimethylsilyl group, respectively. The ¹³C NMR spectrum shows ¹⁸³W coupling to the neopentyl α-carbon (δ 92.9, ¹J_{CW} = 103 Hz) and a smaller coupling the α-carbon of the silacycle (δ 37.1, ¹J_{CW} = 44 Hz). No temperature-dependent dynamic behavior is observed in the proton spectrum over the temperature range of 20 °C to 110 °C. Thus, the structure appears to be static on the NMR time scale.

Complex **16** has not been isolated on a preparative scale to date. However, a concentrated pentane solution of **16** prepared from an NMR tube reaction gave dark

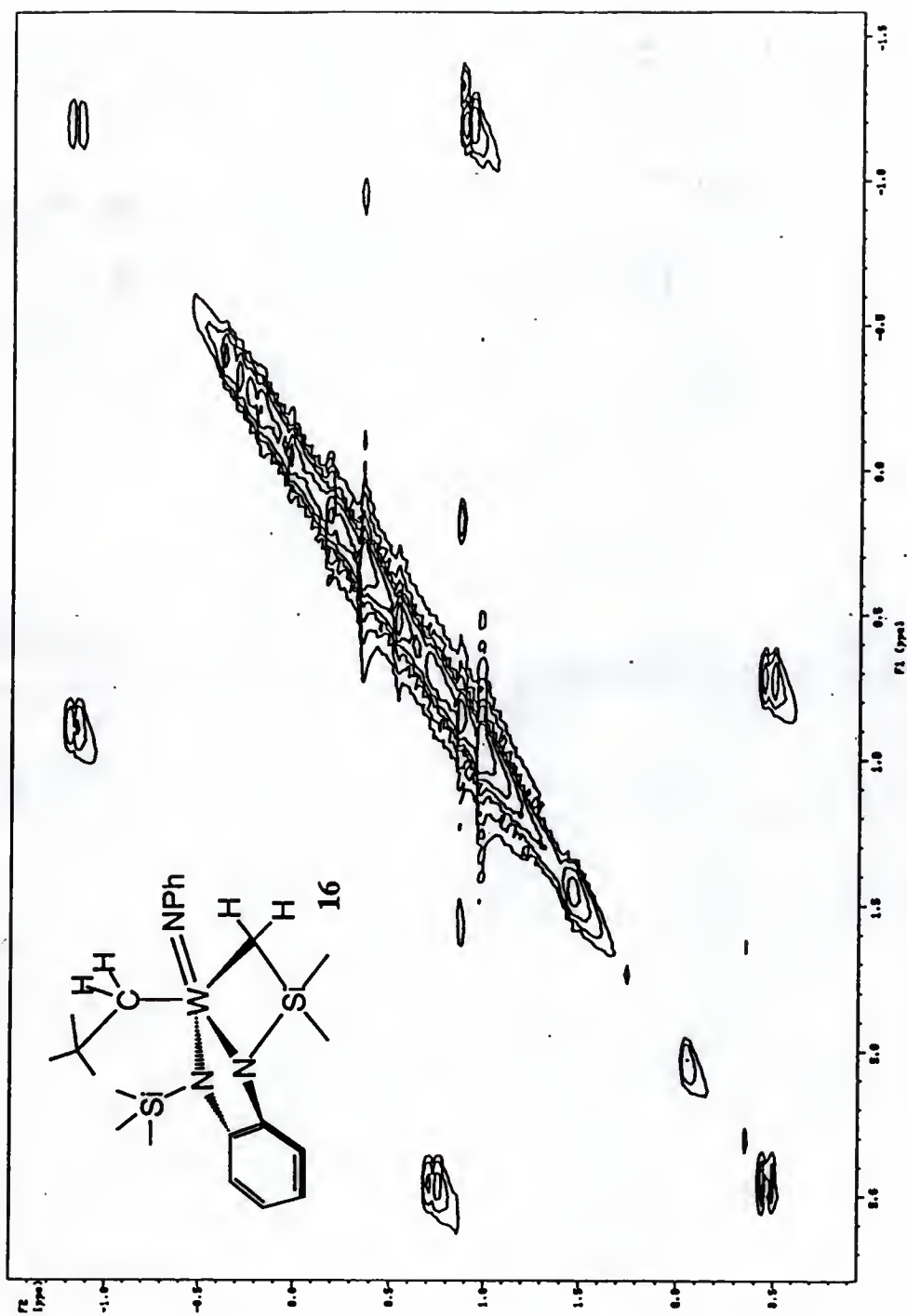


Figure 3.2. 2-D COSY plot of $[(\text{Me}_3\text{SiN})\text{C}_6\text{H}_4(\text{N}'\text{SiMe}_2\text{CH}_2)]\text{W}(\text{NPh})(\text{CH}_2\text{C}(\text{CH}_3)_3)$ (16).

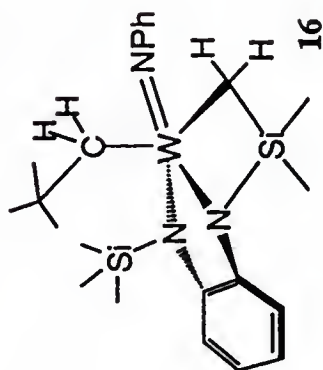


Figure 3.3. ^1H NMR spectrum of $[(\text{Me}_3\text{SiN})\text{C}_6\text{H}_4(\text{N}'\text{SiMe}_2\text{CH}_2)]\text{W}(\text{NPh})(\text{CH}_2\text{C}(\text{CH}_3)_3)$ (16).

yellow-brown single crystals suitable for x-ray diffraction studies, and the solid-state structure of **16** was obtained (Figure 3.4). Selected bond lengths and angles of **16** are given in Table 3.1. The geometry about the tungsten center of **16** is very similar to that of **14**, reported by VanderLende.⁷⁹ The geometry is best described as a square pyramidal structure with the neopentyl ligand in the axial position. The imido nitrogen and the metallated TMS₂pda ligand lie in the basal plane. The tungsten-carbon bond distance of the neopentyl group is 2.12(2) Å and is normal for tungsten-carbon single bonds. The W-C_α-C_β angle of the neopentyl ligand is 128.8(12)°. The tungsten-imido nitrogen bond distance is 1.695(13) Å, and the W-N-phenyl ring bond angle is 157.7(11)°. The phenylenediamido nitrogen-tungsten bonds are similar to those of other TMS₂pda complexes. The tungsten-α-carbon bond distance (2.18(2) Å) for the silacycle is normal for tungsten alkyl bonds.

Table 3.1: Selected Bond Lengths (Å) and Angles (°) for compound **16**.

<u>1</u>	<u>2</u>	<u>3</u>	<u>1-2</u>	<u>1-2-3</u>
N1	W	N2	1.695(13)	144.0(5)
N1	W	N3		96.3(5)
N1	W	C13		105.1(6)
N2	W	N3	2.012(11)	76.7(5)
N2	W	C13		110.5(6)
N2	W	C18		71.9(6)
N3	W	C13	2.039(12)	109.4(6)
N3	W	C18		139.6(6)
C13	W	C18	2.12(2)	105.0(6)
C18	W	N1	2.18(2)	94.6(6)
N2	Si1	C18	1.747(14)	88.1(7)
N2	Si1	C19		113.2(7)
C18	Si1	C19	1.80(2)	114.2(8)
C18	Si1	C20		117.5(8)
N3	Si2	C21	1.766(12)	109.0(7)
N3	Si2	C22		109.3(7)
C1	N1	W	1.45(2)	157.7(11)
W	N2	Si1		104.1(6)
W	N3	Si2		122.0(6)
C14	C13	W	1.49(3)	128.8(12)
W	C18	Si1		95.9(7)

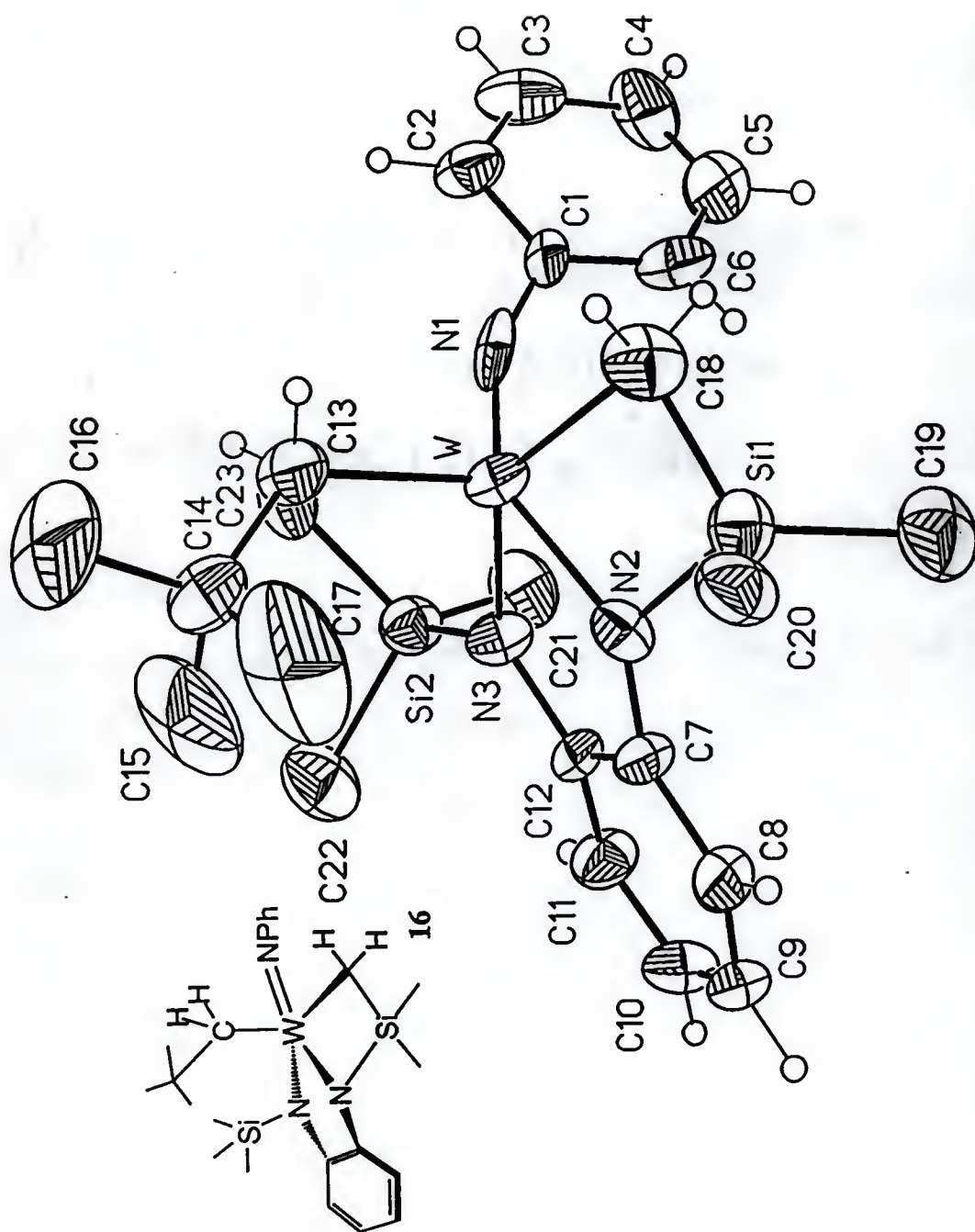


Figure 3.4. Thermal ellipsoid plot of $[(\text{Me}_3\text{SiN})\text{C}_6\text{H}_4(\text{N}'\text{SiMe}_2\text{CH}_2)]\text{W}(\text{NPh})(\text{CH}_2\text{C}(\text{CH}_3)_3)$ (16).

The tungstasilacycle of **16** is related to other compounds reported in the literature. Four-membered metallasilacycles have been formed by γ -abstraction processes.¹⁰⁶ Marks has reported γ -abstraction in bis(cyclopentadienyl)bis(trimethylsilylmethyl)thorium complexes to give a M-C-Si-C ring.^{33,107,108} Likewise, similar chemistry is observed by Diversi for the rhodium and thorium analogues.^{32,109} Perhaps more analogous to the formation of **16**, Andersen reported the γ -C-H activation of bis(trimethylsilyl)amido complexes zirconium and thorium to give M-N-Si-C rings.^{110,111} These processes involve C-H activation by singly bonded nitrogen or carbon atoms. Activation of C-H bonds by the more basic alkylidene ligand have also been reported. Examples are the ϵ -activation of the phenoxide ligand in the tantalum complexes of Rothwell (Figure 1.15)^{112,113} and the orthometallation of a phenyl ring by a tungsten alkylidene reported by Schrock.⁴¹ Both scenarios seem possible for the formation of **16** from **13** or an unobserved alkylidene species, and experiments described later will probe the origin of **16**.

Kinetics of the Formation of the Metallacycle Complex

To begin our investigation of the formation of the silacycle complex, **16**, the kinetics of the thermal decomposition of (TMS₂pda)W(NPh)(CH₂C(CH₃)₃)₂ (**13**) was followed by ¹H NMR spectroscopy. The rate of the decomposition of **13** to give **16** was measured by observing the decreasing peak intensities of the *t*-butyl resonance of the neopentyl ligands (0.99 ppm) and the trimethylsilyl resonance (0.48 ppm) of complex **13** (Figure 3.5a). The decomposition of **13** was found to obey first-order kinetics for up to five half-lives in d₈-toluene over a temperature range of 80 °C to 110 °C. The natural logarithm of the two peak intensities were plotted versus time for at least 3 half-lives (Figure 3.5b). The rates, k_{Np} and k_{TMS} , were taken from the slope, and k_{Np} and k_{TMS} were averaged to give k_{obs} . The rates, k_{Np} and k_{TMS} , agreed to within 3% for each kinetics run. Three kinetic runs were performed at temperatures of 80, 90, 100 and 110

°C, and an average kinetic rate was determined for each temperature. The kinetic data is catalogued in Appendix B.

An Eyring plot was constructed by plotting $\ln(k/T)$ versus $1/T$ (Figure 3.6). The enthalpy of activation ($\Delta H^\ddagger$) was calculated from the slope with the slope equal to $-\Delta H^\ddagger/R$, and the entropy of activation ($\Delta S^\ddagger$) was calculated from the intercept, being equal to $\Delta S^\ddagger/R + 23.76$. For the thermal decomposition of **13** to give **16**, the activation parameters were determined to be $+25.6 \pm 0.3 \text{ kcal mol}^{-1}$ for $\Delta H^\ddagger$ and $-5.4 \pm 0.8 \text{ cal mol}^{-1} \text{ K}^{-1}$ for $\Delta S^\ddagger$. Since $\Delta S^\ddagger$ is determined by extrapolation of a line over a large range, small errors can lead to large variations in entropy terms, and conclusions from these values are limited. However, at this point it will be pointed out that the observed negative entropy agrees with other values determined for cyclometalation reactions, and suggests that in the transition state the rotations of single bonds are restricted and the symmetries of the molecule descends.

One thermolysis experiment was performed in the presence of 7.5 equivalents of neopentane at 90.0 °C and the rate was observed to be $1.15 \times 10^{-4} \text{ sec}^{-1}$. This is significantly slower than the rate without added neopentane ($1.80 \times 10^{-4} \text{ sec}^{-1}$). However, these conditions must be repeated to insure that such a difference is real.

These kinetic studies have given information that should help in the synthesis of **16** on a preparative scale. The ^1H NMR spectra of the kinetic runs indicate that there is a marked increase in decomposition products at 110 °C after five half-lives compared to the reaction at 80 °C after three half-lives. An increase in decomposition products occurs as **16** remains in solution at elevated temperatures. Therefore, in order to isolate the metallacycle on a preparative scale, it is suggested that **13** should be thermolysed in toluene at 80 °C for ten hours or 5 half lives. Immediate evaporation of the toluene, extraction with pentane, and concentration should afford **16** as either a powder or crystals. Coordinating solvents should be avoided since **16** is observed to give alkylidene species in donor solvents.

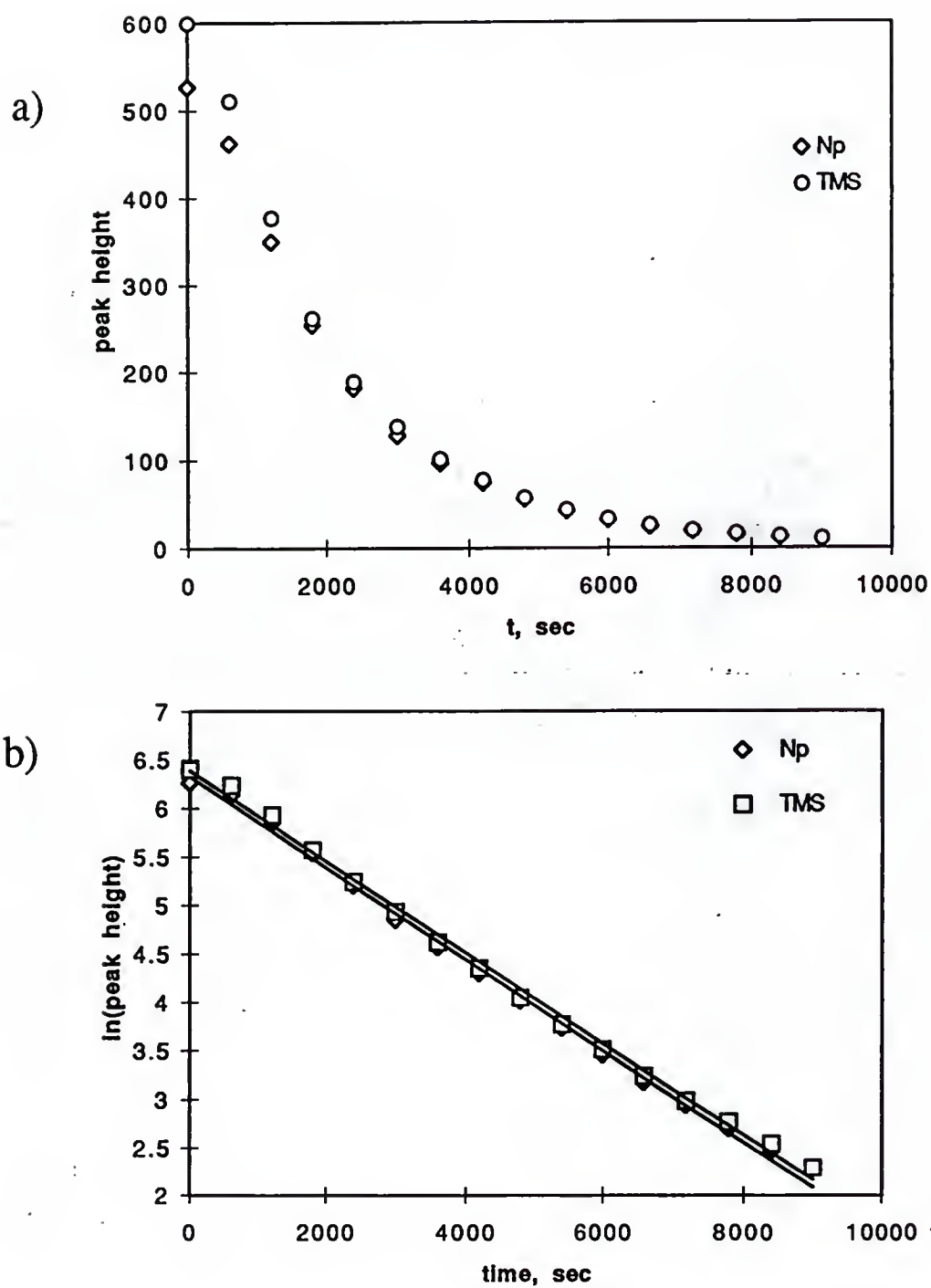


Figure 3.5. Example of Kinetic Data from the Thermolysis of **13**, 100 °C.
 a) Plot of peak heights of NMR resonances of **13** versus time.
 b) First order kinetic plot ($\ln(\text{peak height})$ vs. time) over 5 half lives.

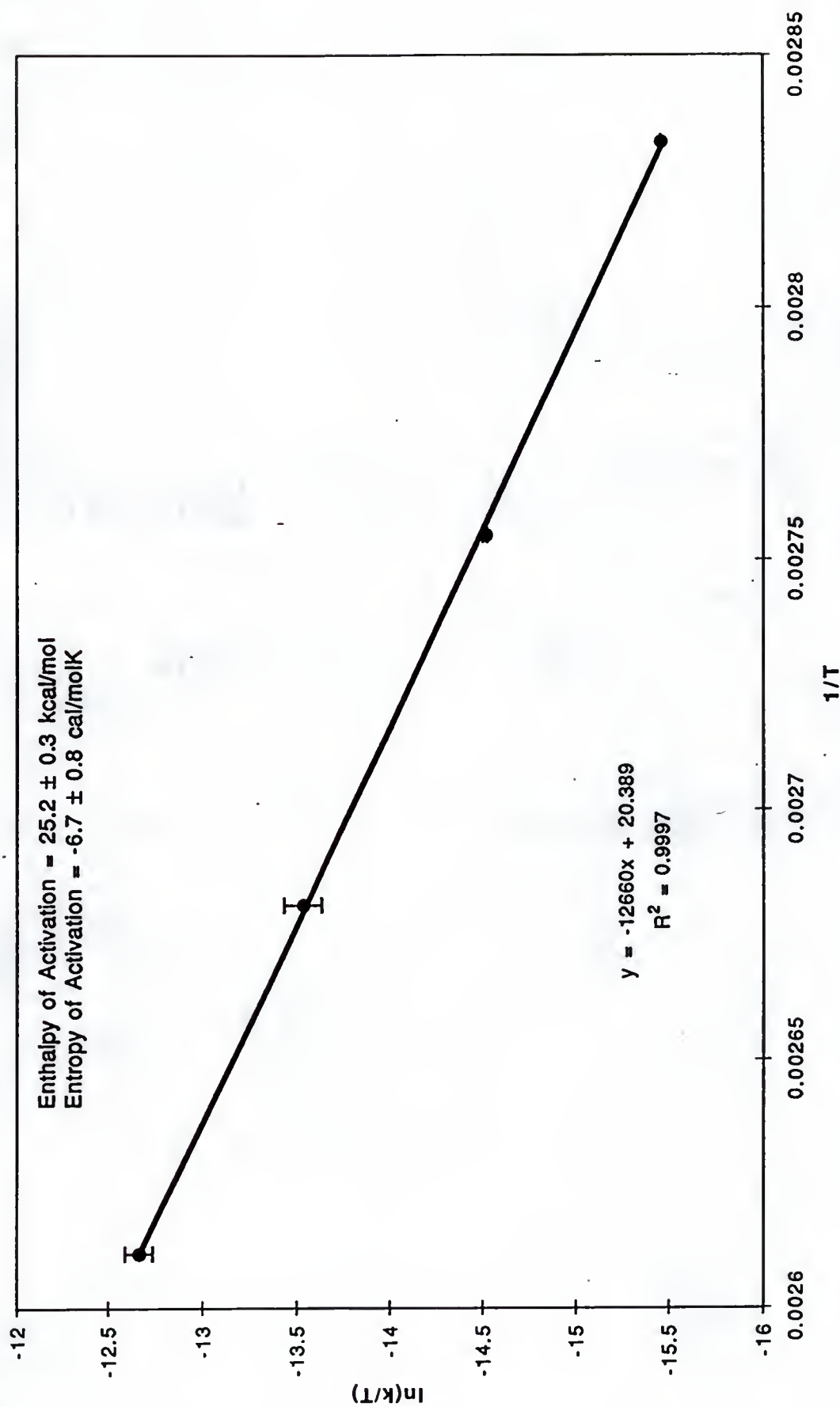


Figure 3.6. Eyring Plot for the Thermolysis of 13 in the Absence of PMe_3 .
Temperature range: 80° C to 110 °C.

Kinetics of the Formation of the Alkylidene Complex

The thermolysis of $(\text{TMS}_2\text{pda})\text{W}(\text{NPh})(\text{CH}_2\text{C}(\text{CH}_3)_3)_2$ (**13**) in the presence of excess PMe_3 gives the tungsten alkylidene complex

$(\text{TMS}_2\text{pda})\text{W}(\text{NPh})(\text{CHC}(\text{CH}_3)_3)(\text{P}(\text{CH}_3)_3)$ (**14**) with coordinated phosphine.

VanderLende reported that the isolation of a Lewis base-alkylidene adduct was only possible with trimethylphosphine.⁸⁴ With PET_3 , a mixture of the metallacycle and the alkylidene-phosphine adduct were observed in the ^1H NMR spectrum. Attempts to prepare analogues of **14** with other Lewis bases (PMePh_2 , PCy_3 , PPh_3 and quinuclidine) were not successful, and only decomposition products or the silacycle **16** was observed.

The kinetics of the formation of **14** were followed over the same temperature range used for the formation of the silacycle complex. The alkylidene complex did demonstrate fluxional behavior over this temperature range. At the temperatures studied, the trimethylsilyl groups interchange faster than the NMR time scale. Thus, a coalesced resonance is observed for the time-averaged trimethylsilyl groups. Variable temperature NMR experiments showed the coalescence temperature of the TMS groups to be 39°C . The rate of exchange at this temperature is calculated to be 44.6 sec^{-1} , and $\Delta G^\ddagger$ is determined to be 15.9 kcalmol^{-1} .¹¹⁴

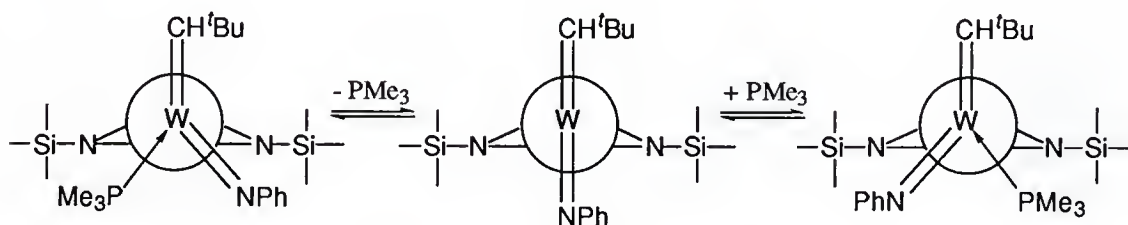


Figure 3.7. Mechanism for the equilibration of the TMS groups of **14**.

The mechanism of the equilibration of the TMS groups is proposed to involve the reversible dissociation of phosphine from the metal center. Complex **14** is an asymmetric molecule. Dissociation of the phosphine ligand induces a plane of symmetry that

equilibrates the TMS groups as shown in Figure 3.7. Once the equilibrium in Figure 3.7 becomes rapid on the NMR time scale, an average resonance is observed for the TMS groups. No phosphine-free adduct is ever observed in the ^1H NMR spectrum.

The kinetics of the formation of **14** were followed in the same manner as the thermolysis of **13**. The rate data for the thermolysis of **13** in the presence of PMe_3 is catalogued in Appendix B. Activation parameters were determined by plotting $\ln(k/T)$ versus $1/T$, and $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were found to be $+28.1 \pm 0.3 \text{ kcal mol}^{-1}$ and $+0.8 \pm 0.8 \text{ cal mol}^{-1}\text{K}^{-1}$, respectively (Figure 3.8). The results indicate that upon addition of PMe_3 the rate of reaction is depressed slightly. A plot of the observed rate constants versus the number of PMe_3 equivalents added is included in Appendix B. Preliminary results indicate that this rate depression is greater at lower temperatures (80°C). At 80°C , the depression of the rate upon adding 20 equivalents PMe_3 is about 30 per cent (0.644 to $0.452 \times 10^{-4} \text{ sec}^{-1}$). It is noted that such a small change in rate is not normally attributed to major changes in the mechanism. The source of this rate depression may be associated with an increase in solvent polarity upon the addition of PMe_3 . For example, the addition of 20 equivalents (0.097 mL) of PMe_3 to 25 mg of **13** in 0.6 mL toluene results in a 15 % v/v solution of the highly polar phosphine. The possibility of this change in rate being due to changing solvent polarity needs to be investigated, and observing the reaction in the presence of deuterated CD_2Cl_2 and CD_3CN is suggested.

A Closer Look at the Role of Phosphine

Trimethylphosphine has not been observed to interact strongly with any of the tungsten bisalkyl complexes with TMS_2pda as the chelating ligand. This seems surprising since $(\text{TMS}_2\text{pda})\text{W}(\text{NPh})(\text{Cl})_2$ (**12**) and a related compound $(\text{TMS}_2\text{dav})\text{W}(\text{NPh})(\text{Cl})_2$ (**17**, TMS_2dav = diamidoveratrole, $(\text{TMSN})_2\text{C}_6\text{H}_2(\text{OCH}_3)_2$) readily react with PMe_3 to give six-coordinate complexes. For compounds $(\text{TMS}_2\text{pda})\text{W}(\text{NPh})(\text{R})_2$ where R is a neopentyl, neophyl, or methyl group, no new resonances are seen in the ^1H NMR that are

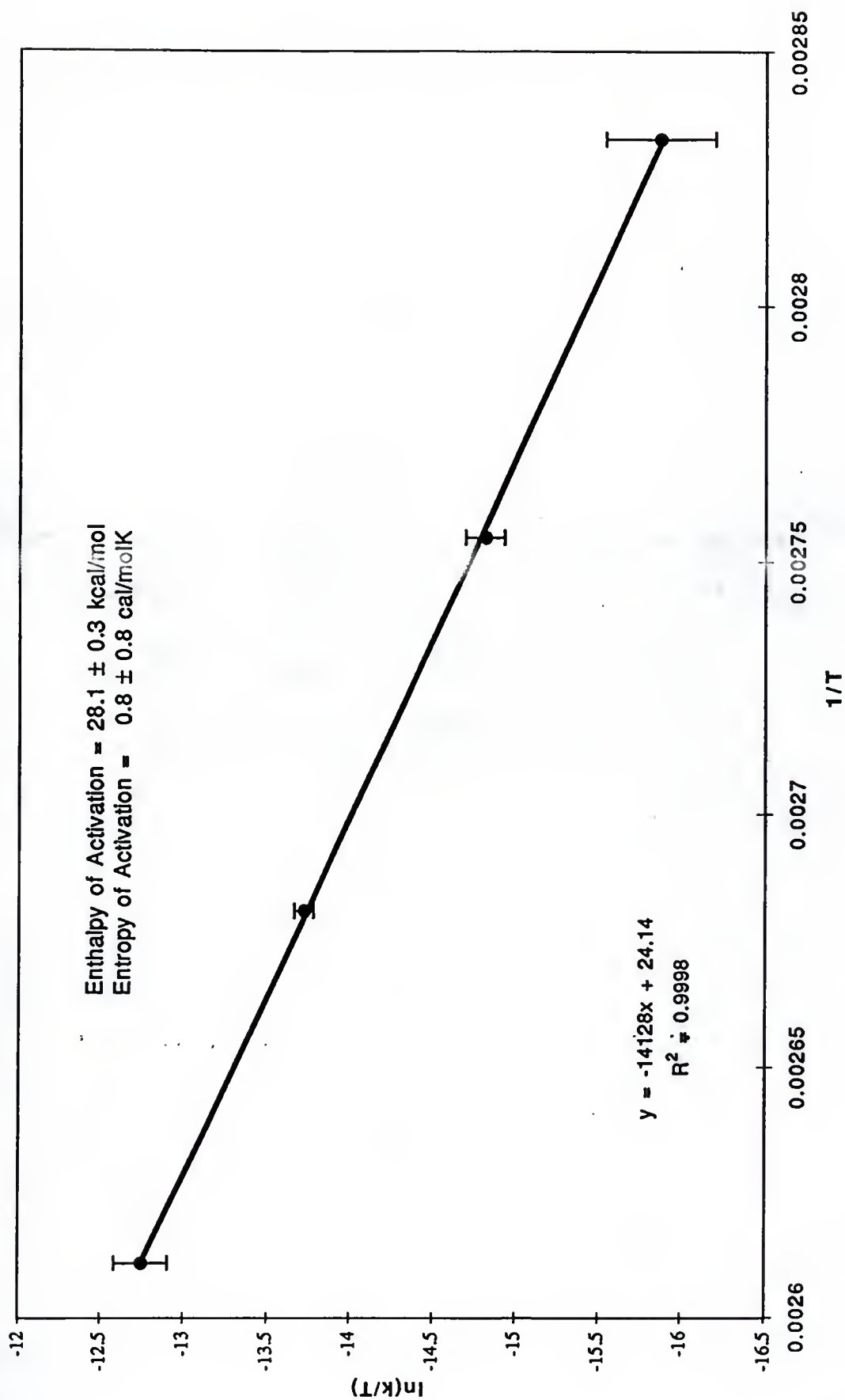


Figure 3.8. Eyring Plot for the Thermolysis of 13 in the Presence of PMe_3 .
 Temperature range: 80°C to 110°C .

attributed to tungsten bisalkyl phosphine complexes. However, the time scale of NMR experiments range from 10^{-1} to 10^{-5} sec $^{-1}$, and therefore the molecules involved in chemical events that occur faster than 10^{-5} sec $^{-1}$ are observed as a time-averaged species.

Ultraviolet-visible (UV-VIS) spectroscopy has a 10^{-14} sec $^{-1}$ time scale limit, and it was proposed that a short-lived bisalkyl phosphine adduct might be detectable by its UV-VIS spectrum. UV-VIS spectroscopy was useful in comparing complexes **12** and **17** and their phosphine adducts. The results of these studies and the observation of **13** in the presence of PMe_3 are described below.

The complexes $(\text{TMS}_2\text{pda})\text{W}(\text{NPh})(\text{Cl})_2$ (**12**) and $(\text{TMS}_2\text{dav})\text{W}(\text{NPh})(\text{Cl})_2$ (**17**) are colored dark yellow to brown in toluene, and upon addition of a coordinating PMe_3 , there is a marked color change to give intensely colored solutions of purple $(\text{TMS}_2\text{pda})\text{W}(\text{NPh})(\text{Cl})_2(\text{PMe}_3)$ (**18**) and blue $(\text{TMS}_2\text{dav})\text{W}(\text{NPh})(\text{Cl})_2(\text{PMe}_3)$ (**19**). These color changes were quantified by observing the visible spectrum of the compounds, and the results are given in the Table 3.2 below.

Table 3.2. UV-VIS Absorbance Data.

Compound	λ_{max} , nm	ϵ , $\text{M}^{-1}\text{cm}^{-1}$	fold angle, °
$(\text{TMS}_2\text{pda})\text{W}(\text{NPh})(\text{Cl})_2$, 12	447	4740	58
$(\text{TMS}_2\text{pda})\text{W}(\text{NPh})(\text{Cl})_2(\text{PMe}_3)$, 18	531	3012	20
$(\text{TMS}_2\text{dav})\text{W}(\text{NPh})(\text{Cl})_2$, 17	486	6759	
$(\text{TMS}_2\text{dav})\text{W}(\text{NPh})(\text{Cl})_2(\text{PMe}_3)$, 19	575	4337	
$(\text{TMS}_2\text{pda})\text{W}(\text{NPh})(\text{CH}_2\text{C}(\text{CH}_3)_3)_2$, 13	393, est. 525	1344, 208	
13 + PMe_3	367, est. 525	1056, 112	

The source of this spectral shift is related to the change in the fold angle of the phenyl ring of the TMS_2pda ligand (Figure 3.9).¹¹⁵⁻¹¹⁷ The fold angle is defined as the 180° complement of the dihedral angle between the plane of the phenyl ring and the plane defined by the W and N atoms of the pda ligand. In the x-ray crystal structures of **12** and **18** the fold angles are 50° and 28° , respectively. Similar changes in the fold angles of **17** and **19** are expected. The folding of the pda ligand is thought to result from the interaction

of the π electrons of the phenyl ring with the d_{z^2} orbital of the five-coordinate metal center. This folding demonstrates the high electrophilicity of the metal center. In the presence of PMe_3 , this interaction is interrupted, and a spectral shift is observed.

One problem with determining if there is a spectral shift from adding PMe_3 to $(\text{TMS}_2\text{pda})\text{W}(\text{NPh})(\text{CH}_2\text{C}(\text{CH}_3)_3)_2$ (**13**) is that pure samples of the bisalkyl complexes are difficult to obtain, and the color of the powders obtained are light yellow-brown at best. Alternatively, washing of **13** with a small portion of acetonitrile affords a good yield of an olive green powder and the ^1H NMR spectrum of the material shows the powder to be cleaner than the brown powders obtained by concentration of pentane solutions. A toluene solution of the olive green powder of **13** is yellow in color and results in a broad maximum in the visible spectrum centered around 525 nm and a UV absorbance is seen at 393 nm. Addition of 1500 equivalents of PMe_3 to **13** results in a blue-shift of the UV absorbance, but a shift of the visible absorbance is not discernible in part due to the broad maximum observed. Addition of 20 equivalents of PMe_3 does not result in a blue shift, but the intensity of all absorbances is reduced. The spectral shift observed for the UV absorbance may be attributable to the change in solvent polarity upon addition of the polar PMe_3 , but source of the bleaching is not evident at this time.

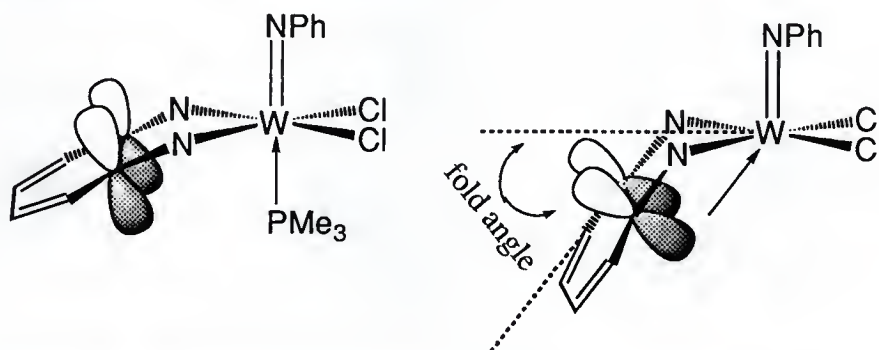


Figure 3.9. Diagram depicting phenyl ring interaction with the metal upon increased fold angle.

Evidence for a phosphine adduct of **13** was also sought by observing the ^{31}P NMR spectra of over a temperature range of $+20\text{ }^\circ\text{C}$ to $-60\text{ }^\circ\text{C}$. For a *dg*-toluene solution of **13** with 1.1 equivalents of PMe_3 , no new resonances were observed in the ^{31}P spectra over

this temperature range. The chemical shift of the free PMe_3 (δ -61.8 at -60 °C) did not change upon addition of the metal complex. The only effect on the spectrum observed was significant broadening of the resonance at -61.8 ppm. The width at half the maximum intensity ($w_{1/2}$) for free PMe_3 is 17.6 Hz. The $w_{1/2}$ values for 1.1 and 2.5 equivalents of PMe_3 are 41.1 Hz and 32.7 Hz, respectively. The trend observed for line broadening upon addition of PMe_3 suggests some interaction of the phosphine with the metal center, but the absence of a difference in chemical shift means that any equilibrium between free and coordinated phosphine lies decidedly towards free phosphine and unbound **13**.

With the absence of a marked interaction between $(\text{TMS}_2\text{pda})\text{W}(\text{NPh})(\text{CH}_2\text{C}(\text{CH}_3)_3)_2$ (**13**) and PMe_3 and only a slight decrease in reaction rates observed with added PMe_3 for the decomposition of **13**, trimethylphosphine is not deemed to be involved in the rate determining step of the formation of $(\text{TMS}_2\text{pda})\text{W}(\text{NPh})(\text{CHC}(\text{CH}_3)_3)(\text{P}(\text{CH}_3)_3)$ (**14**).

Interconversion of the Metallacycle and the Alkylidene Complexes

An interesting result is the observation that the alkylidene complex, $(\text{TMS}_2\text{pda})\text{W}(\text{NPh})(\text{CHC}(\text{CH}_3)_3)(\text{P}(\text{CH}_3)_3)$ (**14**), and metallacycle complex, $[(\text{Me}_3\text{SiN})\text{C}_6\text{H}_4(\text{N}'\text{SiMe}_2\text{CH}_2)]\text{W}(\text{NPh})(\text{CH}_2\text{C}(\text{CH}_3)_3)$ (**16**) can interconvert. Removal of PMe_3 from **14** gives **16** and unidentified decomposition products (Figure 3.10). This reaction has been observed in ^1H NMR experiments with $\text{Cu}(\text{I})\text{Cl}$, MeOTf , and MeI . The cuprous ion acts by irreversibly binding PMe_3 to give an insoluble $\text{CuCl}(\text{PMe}_3)_x$ complex. Cuprous salts are commonly used as "phosphine sponges" to remove phosphines from metal complexes.⁴⁸ The electrophilic methyl groups of MeOTf and MeI act by forming the phosphonium salts, $\text{PMe}_4^+\text{OTf}^-$ or PMe_4^+I^- . The mechanism of this transformation to give **16** supposedly gives a phosphine-free alkylidene complex, $(\text{TMS}_2\text{pda})\text{W}(\text{NPh})(\text{CHC}(\text{CH}_3)_3)$ (**20**). This four-coordinate complex **20** can then activate a C-H bond of a TMS group of the pda ligand to give the silacycle complex, **16**.

The γ -C-H activation by an alkylidene ligand proposed is preceded in the literature by the examples mentioned earlier in this chapter. These methods have not proven effective in the preparation of **16** on a large scale.

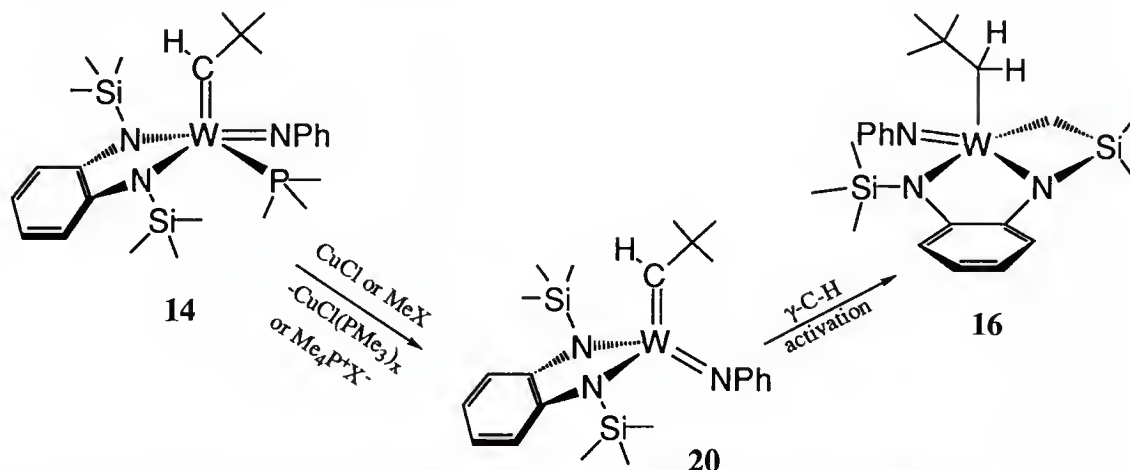


Figure 3.10. Proposed mechanism of PMe_3 abstraction of **14** to give **16**.

The silacycle complex **16** can also be converted to the alkylidene complex **14**. Addition of excess PMe_3 to a dark yellow d δ -toluene solution of **16** quantitatively gives an orange solution of **14** over two hours at ambient temperatures (Figure 3.11). Considering the fact that removal of the PMe_3 from **14** gives **16**, the mechanism of the reverse reaction is hypothesized to consist of an equilibrium between **16** and the four-coordinate alkylidene complex **20**. This equilibrium decidedly favors **16** in solution, but the PMe_3 present in solution effectively traps **20** as the phosphine-bound alkylidene complex **14**. As a result, the equilibrium of **16** and **20** is driven towards the formation of the alkylidene, and the alkylidene complex **14** is formed quantitatively since the binding of PMe_3 to **20** is essentially irreversible at ambient temperatures.

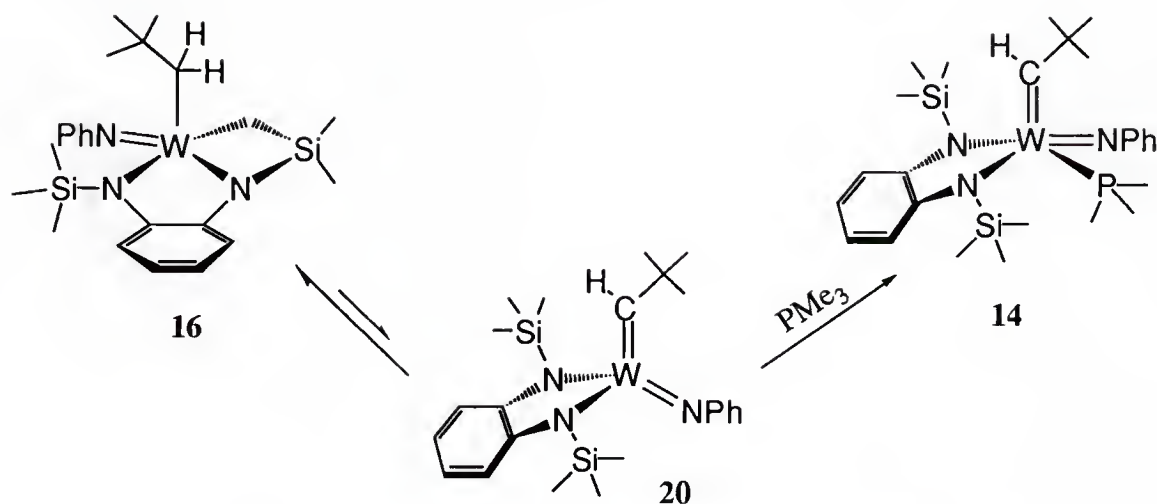


Figure 3.11. Proposed mechanism of PMe_3 addition to **16** to give **14**.

Deuteration studies described below suggest that **16** is in equilibrium with **20**, however the existence of this equilibrium has not been rigorously demonstrated. The interconversions of **14** and **16** are amenable to kinetic study, and the following experiments are planned. The homogeneous reaction of **14** and MeOTf or MeI will be studied by varying the concentration of the electrophiles over a temperature range. This study should define the molecularity and rate law for the abstraction of phosphine and rearrangement to give the silacycle. Likewise, the kinetics of reacting **16** with varying concentrations of PMe_3 over a temperature range will also demonstrate the dependence of the reaction on PMe_3 . Rigorous study of this process is contingent upon the preparation of pure **16**. Another experiment to demonstrate a dynamic equilibrium between **16** and **20** is spin saturation transfer studies with ^1H NMR spectroscopy. T_1 measurements of the silyl methyls groups were on the order of 1.2 seconds. Spin saturation transfer experiments at 20 and 110 $^\circ\text{C}$ did not demonstrate a dynamic equilibrium between **16** and **20**.

Deuterium-Labeling Studies

In order to decide whether α -abstraction or γ -abstraction pathways are occurring to give the alkylidene complex, **14**, and the metallasilacycle complex, **16**, deuterium-labeling

experiments were performed by employing $(\text{TMS}_2\text{pda})\text{W}(\text{NPh})(\text{CD}_2\text{C}(\text{CH}_3)_3)_2$ (**13-*d*₄**). Complex **13-*d*₄** was prepared by alkylating $(\text{TMS}_2\text{pda})\text{W}(\text{NPh})(\text{Cl})_2$ (**12**) with two equivalents of α,α' -dideuterioneopentyl magnesium chloride, $\text{Mg}(\text{CD}_2\text{C}(\text{CH}_3)_3)\text{Cl}$.^{118,119} The results were followed by mass spectrometry of the neopentane by-products and ^2H NMR spectroscopy.

Chemical Ionization Mass Spectrometry Study

Analysis of deuterated neopentane by-products ($\text{NpH-}d_n$) by mass spectrometry has been reported as a method to determine whether α -abstraction or γ -abstraction pathways are operative in the formation of alkylidene and metallacycle complexes. The seminal account of this method was by Schrock in his investigation of the role of α -abstraction in forming $\text{Ta}(\text{CHC}(\text{CH}_3)_3)(\text{CH}_2\text{C}(\text{CH}_3)_3)_3$.³⁸ Marks, using the same method, has demonstrated that γ -abstraction is the major pathway for the decomposition of $\text{Cp}_2\text{Th}(\text{CH}_2\text{C}(\text{CH}_3)_3)_2$ to give the metallacycle $\text{Cp}_2\text{Th}(\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2)$.¹⁰⁸

These labeling studies are especially important to this research because in the previous section the interconversion of the alkylidene and silacycle complexes was noted. Therefore the origin of either species might arise from an initial α - or γ -abstraction pathway followed by an interconversion mechanism. Evidence for the two pathways is presented below.

For an initial α -abstraction pathway involving **13-*d*₄**, the neopentane by-product produced would have the formula $\text{C}(\text{CH}_3)_3(\text{CD}_3)$, or $\text{NpH-}d_3$ (Figure 3.12). This is the only pathway that would result in $\text{NpH-}d_3$ from the decomposition of **13-*d*₄**.

For an initial γ -abstraction pathway involving **13-*d*₄**, the neopentane by-product produced would have the formula $\text{C}(\text{CH}_3)_3(\text{CHD}_2)$, or $\text{NpH-}d_2$ (Figure 3.13). Formation of $\text{NpH-}d_2$ from the decomposition of **13-*d*₄** would not distinguish between γ -abstraction pathways involving activation of the γ -C-H bonds of the TMS group of the pda ligand or the *tert*-butyl group of the neopentyl ligand. However, with no evidence for the existence

of $(\text{TMS}_2\text{pda})\text{W}(\text{NPh})(\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2)$ (**15**), it will be assumed that any $\text{NpH-}d_2$ formed results from the activation of a TMS group to give **16**.

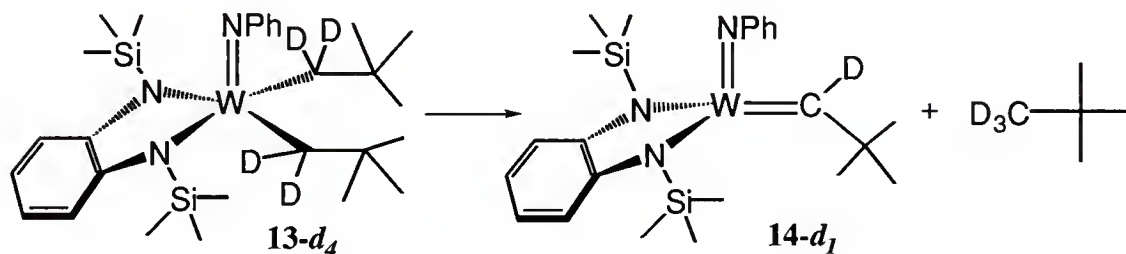


Figure 3.12. Formation of $\text{NpH-}d_3$ via the α -abstraction pathway.

The thermolysis of **13- d_4** was performed at 80 °C and 100 °C with and without added PMe_3 . Also, deuterated and non-deuterated solvents were used in order to determine whether C-H(D) activation of the solvent by **13- d_4** is significant. After thermolysis, the volatiles of the reaction ($\text{NpH-}d_n$, PMe_3 , solvent) were distilled from the reaction mixture in order to eliminate possible secondary reactions catalyzed by any metal species present.

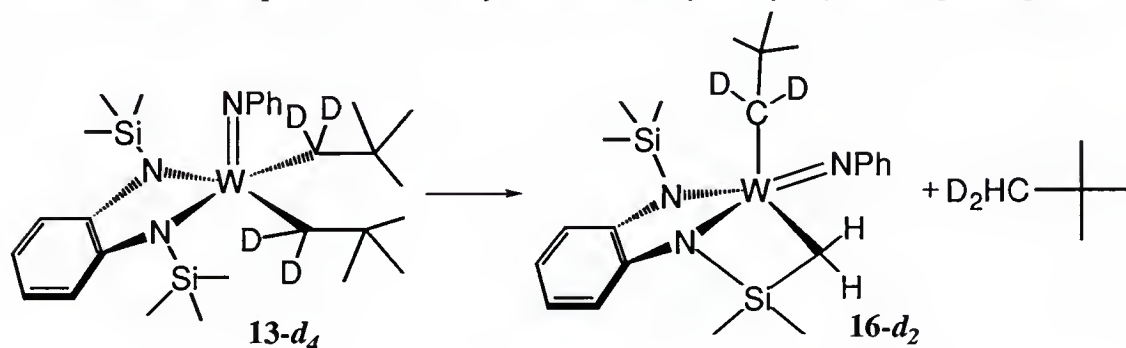


Figure 3.13. Formation of $\text{NpH-}d_2$ via the γ -abstraction pathway.

The volatiles were separated and analyzed by GC-MS techniques. Chemical ionization (CI) by methane was used to generate charged analytes. For neopentane, CI generates *tert*-butyl cations as the major ion observed. Thus, $\text{NpH-}d_3$ generates ions with m/z values of 60 and 57 in a 3:1 ratio, and $\text{NpH-}d_2$ generates ions with m/z values of 59 and 57 in a 3:1 ratio. A molecular envelop for m/z values of 72 to 75 is also observed and is attributed to neopentyl cations resulting from the loss of dihydrogen from the protonated

neopentane generated. For this study, the *t*-butyl cation envelop was used to determine whether α - or γ -abstraction is operative. Other studies have utilized electron impact techniques (EI) to generate *t*-butyl cations. At the outset of this study, CI was favored over EI because CI is a gentler ionization technique. Despite the fact that CI is a "softer" ionization technique, protonated neopentane readily eliminates methane to give the observed *t*-butyl cations. Fortunately, there is no scrambling of protons and deuterons in the *t*-butyl cations generated.

Table 3.3 summarizes the results of the CIMS data. The % NpH- d_n values given are calculated from the relative m/z peak height of NpH- d_n corrected for ^{13}C abundance divided by the sum of the relative m/z peak heights of NpH- d_2 and NpH- d_3 given in Appendix B. In Table B, the peak heights at m/z values of 58 and 61 result from the ^{13}C isotopes.

Table 3.3. Relative Amounts of NpH- d_n Produced in Thermolysis Reactions.

Entry	temp, solvent	PMe ₃ , equiv.	% NpH- d_2	% NpH- d_3
1	80 °C, C ₆ D ₆	0	33	67
2	80 °C, C ₇ H ₈	0	36	64
3	80 °C, C ₇ H ₈	5	16 (± 2)	84 (± 2)
4	100 °C, C ₇ D ₈	0	40	60
5	100 °C, C ₇ D ₈	20	8 (± 1)	92 (± 1)
6	110 °C, C ₇ H ₈	0	45	55
7	25 °C, C ₆ D ₆	H ₂	93	7

Table 3.3 gives the CIMS data to date, and reactions will be repeated as necessary to increase the confidence in these results. Samples of NpH- d_2 and NpH- d_3 prepared by the reaction of Mg(CD₂C(CH₃)₃)Cl with CH₃OH or CH₃OD, respectively. These samples were submitted for CIMS, but their concentrations were not high enough to observe the ^{13}C isotope peaks. New samples of NpH- d_2 and NpH- d_3 will be submitted, and with their known fragmentation patterns, the CIMS data can be modeled and treated rigorously.

Comparing entries 2 to 3 and 4 to 5 does demonstrate the marked increase in the relative ratio of NpH- d_3 to NpH- d_2 upon the addition of PMe₃ to the thermolysis reaction. The degree of the increase appears to increase upon increasing the temperature and PMe₃ concentration, but this difference has not been shown to be significant due to the lack of data. Also, performing the reaction in a non-deuterated solvent shows a trend of increased NpH- d_2 production. This trend suggests that C-H activation of the solvent by **13- d_4** may occur to a minor extent, but this trend too must be confirmed with further analysis. Entry 7 is for the hydrogenolysis of **13- d_4** . This reaction demonstrates that the tungsten alkyl bond can participate in σ -bond metathesis, and the more nucleophilic alkylidene ligand may not be necessary for C-H bond activation. With the limited data gathered, the α -abstraction pathway is favored over the γ -abstraction pathway, and addition of PMe₃ increases the relative rate of α -abstraction versus γ -abstraction.

Deuterium NMR Spectroscopy

The thermolysis reactions of **13- d_4** were also analyzed by ²H NMR spectroscopy. The most striking result from the spectra is observed scrambling of deuterons into the TMS groups of the alkylidene complex **14** and the metallacycle complex **16**. In fact, it was this observation that eventually led to a reassignment of the metallacycle structure as **16** and not **15**.

The α,α' -deuterons of complex **13- d_4** give rise to a single broad signal at δ 2.25 (Figure 3.14a). After thermolysis of a d_0 -toluene solution of **13- d_4** at 110 °C for 90 minutes, several new signals are present (Figure 3.14b). Most prominent is a large singlet at δ 0.95 assigned to the NpH- d_n formed. Three broad, overlapping signals are observed at δ 0.70, 0.53 and 0.36. These signals are approximately in a 1:3:1 ratio and assigned as the β and β' methyl groups of the silacycle and the free trimethylsilyl group. No deuterium signals are observed corresponding to the silacycle or neopentyl methylene positions, but the signal-to-noise ratio (S/N) for their resonances may obscure their observation. A

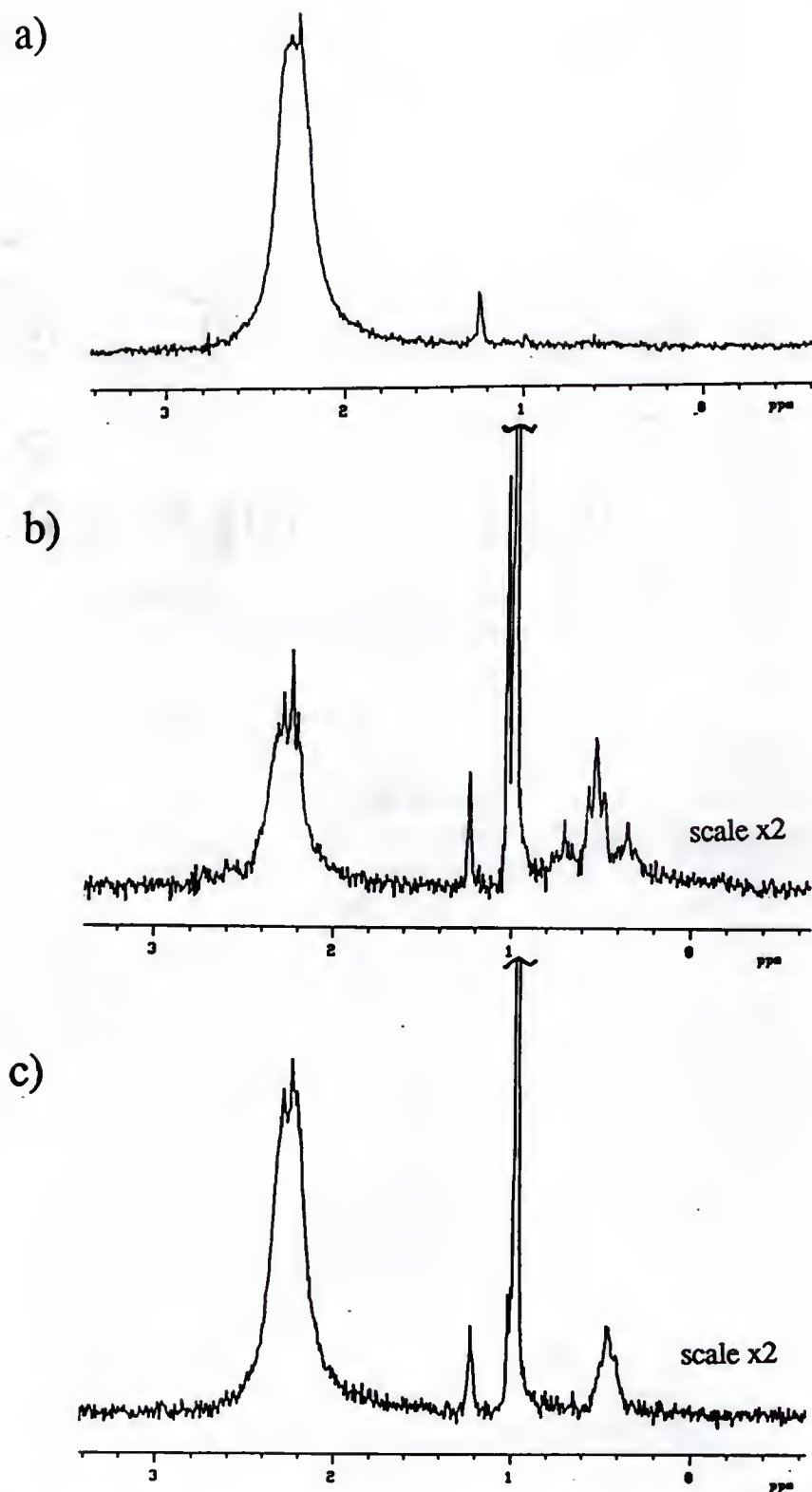


Figure 3.14. ^2H NMR spectra. a) Complex 13- d_4 before thermolysis.
b) Product from thermolysis in absence of PMe_3 .
c) Product from thermolysis in presence of PMe_3 .

'doublet', which overlaps with the NpH resonance, is also observed at δ 1.01. Its assignment is not clear at present, but the *t*-butyl groups of the neopentyl ligands of **13** and **16** give ^1H NMR signals at δ 1.00 and 1.02, respectively.

The ^2H NMR spectrum of the thermolysis reaction of **13-*d*₄** with excess PMe_3 shows similar features (Figure 3.14c). A large singlet for NpH-*d_n* is observed, and a single broad resonance at δ 0.41 is assigned to the TMS groups of the alkylidene complex, **14**. No deuterium signal is observed that would correspond to an α -deuteron on the alkylidene ligand. The same unassigned doublet at δ 1.01 is observed as in the thermolysis reaction without PMe_3 , but the doublet is of lesser intensity for the PMe_3 case. The alkylidene *t*-butyl group gives a ^1H NMR signal at δ 0.98.

The observation of complete scrambling of deuterons to all silicon methyl positions suggests that an equilibrium between the metallacycle complex **16** and the unbound alkylidene complex **20** exists. In the case of added PMe_3 , this equilibrium exchange may also be faster than PMe_3 coordination to **20** to give **14**. However, the additional experiments described in the section on the interconversion of **14** and **16** are needed to confirm these statements. The doublet observed at δ 1.01 in both thermolysis reactions may suggest a mechanism to exchange the α -methylene positions of the neopentyl ligand with the *t*-butyl group of that same ligand.

Kinetic Isotope Effects in the Formation of the Metallacycle and the Alkylidene Complexes

The complex **13-*d*₄** also allows investigation of the mechanism by determining if a kinetic isotope effect (KIE) is observed. Primary kinetic isotope effects have been reported in the literature for α -abstraction and γ -abstraction pathways. The relative rates of reaction of the protonated versus deuterated analogues ($k_{\text{H}}/k_{\text{D}}$) is typically on the order of 6 when C-H(D) breaking is involved in the rate determining step.^{50,108,118,120}

From the kinetic data tabulated in Appendix B, the value for k_H/k_D was determined to be 5.2 ± 0.9 for the thermolysis of **13** in the presence of 20 equivalents of PMe_3 . The value of k_H/k_D for the thermolysis of **13** in the absence of PMe_3 is 3.9 ± 0.4 .

Based on results from the CIMS studies, the KIEs measured reflect a mixture of two competing pathways, α - and γ - abstraction. For **13-d₄**, α -abstraction involves the breaking of a C-D bond, but γ -abstraction involves the breaking of a C-H bond. Therefore, only the α -abstraction pathway will incur a primary KIE. No primary KIE is expected for the γ -abstraction pathway, and a secondary KIE should not be appreciable since no changes in hybridization occur. The KIEs measured are

$$\frac{k_H}{k_D} = \frac{k_{H\alpha} + k_\gamma}{k_{D\alpha} + k_\gamma} \quad (1)$$

The NpH-d_n product ratio determined by CIMS relates the relative rates of $k_{D\alpha}$ and k_γ as

$$\frac{\text{NpH-d}_3}{\text{NpH-d}_2} = \frac{k_{D\alpha}}{k_\gamma} \quad (2)$$

Solving for $k_{D\alpha}$ in equation (2) and substitution into equation (1) allows for the $k_{H\alpha}/k_\gamma$ ratio to be determined. For thermolysis in the presence of PMe_3 , $k_{H\alpha}/k_\gamma$ is 64 ± 14 . In the absence of PMe_3 , $k_{H\alpha}/k_\gamma$ is 9 ± 2 for a preliminary KIE of 3.9 ± 0.4 .

Rearrangement and substitution of (1) with (2) give the equation

$$\frac{k_H}{k_D} = \left(\frac{k_{H\alpha}}{k_{D\alpha}} \right) \left(\frac{\text{NpH-d}_3}{\text{NpH}_{\text{total}}} \right) + \left(\frac{k_\gamma}{k_\gamma} \right) \left(\frac{\text{NpH-d}_2}{\text{NpH}_{\text{total}}} \right) \quad (3)$$

and solving for $k_{H\alpha}/k_{D\alpha}$, the actual KIE for α -abstraction can be extracted from the data. In the presence of PMe_3 , $k_{H\alpha}/k_{D\alpha}$ is determined to be 5.6 ± 1.0 . In the absence of PMe_3 , $k_{H\alpha}/k_{D\alpha}$ is determined to be 5.8 ± 0.5 .

Proposed Mechanistic Scheme

Considering the experiments described above, a mechanistic scheme can be proposed to explain our observations. Further investigation will be necessary to increase support for the proposed mechanisms and to expand their details.

The key points of the following scheme are as follows. Competing α - and γ -abstraction pathways from the bisalkyl complex **13** compose the rate determining steps. Trimethylphosphine is not implicated in the rate determining steps, but the ligand does serve to trap the alkylidene complex **20**. Also, a process capable of interconverting the alkylidene and metallasilacycle complexes is incorporated. The scheme is given in Figure 3.15 below, and the supporting observations are summarized.

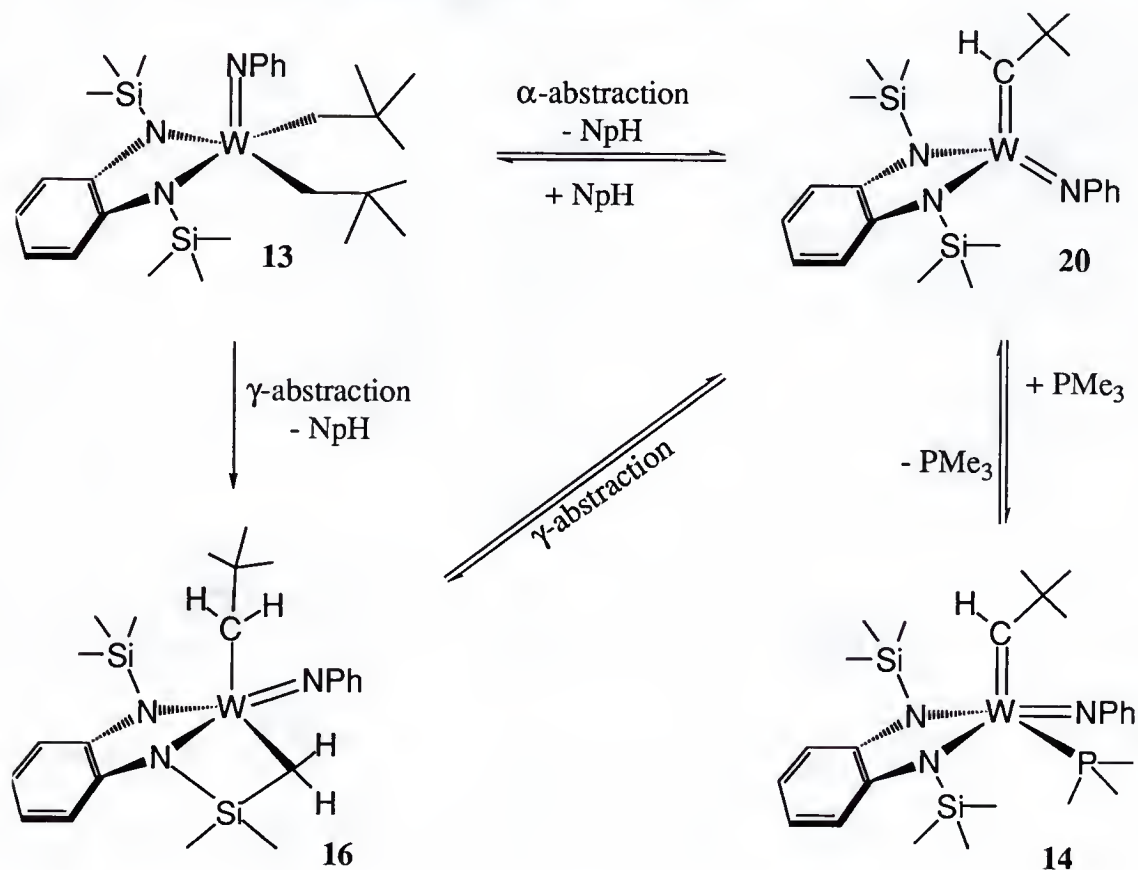


Figure 3.15. Proposed mechanistic scheme.

The reversible α -abstraction process interchanging **13** and **20** is supported by the following observations. A significant kinetic isotope effect (KIE) was observed for the

thermolysis reactions involving **13-*d*₄**. The k_H/k_D of 5.2 ± 0.9 determined for thermolysis in the presence of phosphine is in agreement with other values reported in the literature where α -abstraction mechanisms are operative. The CIMS analyses of the volatiles of the reactions showed NpH-*d*₃ to be the major isotopomer of neopentane. No other pathway besides α -abstraction would result in the formation of NpH-*d*₃. The reversible α -abstraction process proposed provides a pathway by which the α -deuterons of **13-*d*₄** can interchange with the γ -carbons of the neopentyl ligand. The possibility of such an interchange is suggested by ²H NMR spectra which show resonances at δ 1.01.

Evidence for the competitive γ -abstraction includes the production of NpH-*d*₂ during the thermolysis reactions, and it is noted that in the absence of PMe₃, the relative ratio NpH-*d*₃ and -*d*₂ decreases markedly. As well, initial KIE results for the thermolysis reaction in the absence of PMe₃ give a k_H/k_D of 3.9 ± 0.4 , and this lower observed value agrees with the change in NpH-*d_n* ratio.

The equilibrium postulated that interconverts the metallacycle **16** and the unbound alkylidene complex **20** is necessary for the scheme due to several observations. Whether PMe₃ is present or not, both α - and γ -abstractions occur, and interconversion of **16** and **20** must occur in order to achieve the yields of **14** or **16** obtained. Thus, in the absence of PMe₃, the alkylidene complex **20** formed by α -abstraction must convert to the metallacycle complex **16**. An equilibrium mechanism is also the most straight forward way by which the α -deuterons of **13-*d*₄** can interchange with the silicon methyl substituents of the pda ligand. The ability to interconvert **14** and **16** by either the abstraction of the bound PMe₃ of **14** or the addition of PMe₃ to **16** indicates the relationship of the metallacycle and alkylidene complexes. This interconversion of **14** and **16** is amenable to further kinetic study, and the results will add detail to this aspect of the scheme.

The lack of any strong evidence for the interaction of PMe₃ with **13** precludes its involvement in the rate determining steps, and the proposed scheme relegates its role to the trapping of the four-coordinate alkylidene complex **20**. Trimethylphosphine does alter the

relative ratio of deuterated neopentane produced and the observed rates of reaction. It has been suggested that these slight changes for the reaction may be due to subtle solvent polarity effects, and the fact that these changes are slight does not support major changes in the mechanistic scheme upon the addition of phosphine.

Conclusion

In choosing an ancillary chelating ligand to stabilize alkylidene, a requirement that is often taken for granted is that the ligand does not react with the alkylidene ligand. The situation with the TMS_2pda tungsten complexes in this chapter was surprising, but not totally unexpected considering literature precedence. However, the chemistry presented has led to a unique opportunity to begin study of the C-H activation potential of alkylidene ligands. The TMS_2pda ligand was initially chosen because of its facile synthesis compared to other N,N'-disubstituted pda ligands. With the identity of the metallacycle established and some understanding of the interconversion between the metallacycle and alkylidene complexes, altering the substituents of pda ligands will possibly lead to new chemistry favoring either formation of metallacycles or alkylidene complexes. Without the studies presented in this chapter, extremely little was known about the nature of the complexes being formed and used for polymerizations. Now more information is known, and new ideas are presenting themselves.

CHAPTER 4 EXPERIMENTAL PROCEDURES

Materials and Methods

All syntheses were performed under dry argon atmosphere using standard Schlenk techniques. Tetrahydrofuran (THF), diethyl ether (Et₂O), toluene, and pentane were distilled from potassium or sodium benzophenone ketyl; dichloromethane (CH₂Cl₂) was distilled from P₂O₅. Methanol and acetonitrile were dried over 3 Å molecular sieves. Deuterated solvents were freeze-thaw degassed three times and stored over molecular sieves under argon. Mo(CHC(CH₃)₂Ph)(NAr)(OTf)₂(DME)₄₂, potassium hydrotris(1-pyrazolyl)borate (KTP),⁸⁰ HBAr'₄ · Et₂O (Ar' = 3,5-C₆H₃(CF₃)₂),⁹⁷ trityl tetrakis(pentafluorophenyl)borate,⁹⁴ and tris(pentafluorophenyl)boron⁹⁵, Mg(CD₂C(CH₃)₃)Cl¹¹⁸ and TMS₂pdaW(NPh)Cl₂⁷⁹ were prepared according to literature methods.

¹H, ²H, ¹³C, ¹⁹F, ²⁹Si and ³¹P NMR spectra were recorded on a Varian VXR-300, a Varian Gemini-300 or a General Electric QE-300 spectrometer. Elemental analyses were performed by the University of Florida Department of Chemistry Analytical Services. IR spectra were recorded on a Perkin Elmer 1200 series spectrometer in KBr pellets which were prepared under N₂ unless otherwise noted. GPC analyses were carried out with the use of Phenomenex Phenogel 5 500Å and 5000Å coupled columns, a Waters Associates differential refractometer, and a Perkin Elmer LC-75 spectrophotometric detector on polymer samples 0.1 - 0.3 % w/v in THF. The GPC columns were calibrated versus commercially available 1,4-polybutadiene standards ranging from 430 to 25,000 g/mol.

SynthesesTpMo(CHC(CH₃)₂Ph)(NAr)(SO₃CF₃) (1)

Mo(CHC(CH₃)₂Ph)(NAr)(OTf)₂(DME) (3.53 g, 4.46 mmol) and KTp (1.21 g, 4.81 mmol) were stirred in 100 ml THF at room temperature under argon. A yellowish brown solution resulted after 3 hours, and the solvent was removed under reduced pressure. The product was extracted with Et₂O leaving white KOTf solids. Solvent removal, followed by washing with pentane at 0°C, gave **1** as yellow solids (2.91 g, 3.82 mmol, 85.6% yield). The product may be recrystallized from Et₂O.

¹H NMR(C₆D₆, 22°C): δ 14.73 (s, 1 H, CHC(CH₃)₂Ph); 9.19, 7.70, 7.22, 7.09, 6.99, 6.22 (each a d, 1 H each, Tp ring H's, 3,5-positions); 7.34-6.66 (m, 8 H, Ph, Ar); 5.84, 5.65, 5.49 (t, 1 H each, Tp ring H's, 4-position); 4.81, 2.50 (each a broad sept, 1 H each, CH(CH₃)₂); 2.42, 1.86 (each a s, 3 H each, CHC(CH₃)₂Ph); 1.67, 0.79, -0.06 (each a broad d, 6:3:3 H, CH(CH₃)₂). ¹³C NMR δ 333.0 (¹J_{CH} = 120 Hz, CHC(CH₃)₂Ph); 148.2, 144.0, 141.6, 137.2, 135.1, 134.8, 129.3, 129.0, 128.9, 126.7, 126.26, 106.4, 105.9, 105.4 (Tp, Ph, Ar); 56.6 (CHC(CH₃)₂Ph); 31.2, 30.3, 28.4, 28.2, 26.1, 23.9, 23.7, 23.0 (CH(CH₃)₂, CHC(CH₃)₂Ph). IR: ν_{BH} = 2523 cm⁻¹; ν_{S=O} = 1202, 633 cm⁻¹. Elemental analysis calculated for C₃₂H₃₉BF₃MoN₇O₃S: C, 50.21; H, 5.14; N, 12.81. Found: C, 49.96; H, 5.01; N, 12.71.

TpMo(CH₂C(CH₃)₂Ph)(NAr)(O) (2)

1 ml of water was added to a yellow solution of **1** (0.172g, 0.225mmol) in 50 ml Et₂O over 5.0g of Florisil. After stirring 24h at room temperature, the solution became orange and the slurry was filtered. The solvent and excess H₂O were removed under reduced pressure to give orange solids. ¹H NMR showed **1** was present (10%). The product was recrystallized from pentane to give orange crystals. (0.098g, 0.155 mmol, 69% yield). Alternatively, **1** (0.098g, 0.128 mmol) in 10 ml of THF was added to a

stirring mixture of CsOH·H₂O (0.025g, 0.149 mmol) in 50 ml THF at room temperature. After 12 hours, the solution became orange-yellow. The THF was removed under reduced pressure, and the product was extracted in pentane leaving white solids. Solvent removal resulted in an orange solid. ¹H NMR showed that **1** had been quantitatively converted to **2**. ¹H NMR: δ (8.35, 7.90, 7.42, 7.31, 7.24, 7.10 (each a d, 1 H each, Tp ring H's, 3,5-positions); 7.55 - 7.00 (m, 8 H, Ph, Ar); 5.93, 5.79, 5.37 (each a t, 1 H each, Tp ring H's, 4-position); 4.63 (broad m., 2 H, CH(CH₃)₂); 3.27, 2.87 (each a d, 1 H each, ²J_{HH} = 13 Hz, CH₂C(CH₃)₂Ph); 1.87, 1.81 (each a s, 3 H each, CH(CH₃)₂); 1.35, 0.93 (each a d, 6 H each, CH(CH₃)₂). ¹³C NMR: δ 154.1, 152.7, 151.2, 144.2, 143.5, 143.0, 136.1, 134.7, 134.3, 130.0, 128.2, 126.3, 125.1, 123.6, 105.9, 105.7, 104.8, 71.1 (¹J_{CH} = 125.1 Hz, CH₂C(CH₃)₂Ph), 43.0, 32.6, 32.4, 27.6, 24.6, 23.7. IR: ν_{Mo=O} = 896 cm⁻¹. Elemental analysis calculated for C₃₁H₄₀BMoN₇O: C, 58.78; H, 6.36; N, 15.48. Found: C, 58.60; H, 6.40; N, 15.10.

TpMo(CHC(CH₃)₂Ph)(NAr)(OCH₃) (**4**)

5 g of Florisil was slurried for one hour in dry methanol. Compound **1** (0.475 g, 0.620 mmol) was dissolved in 3 mL of Et₂O and transferred to the Florisil slurry giving a faint yellow solution. After stirring at room temperature for 24 hours, the mixture was filtered and the methanol solution was reduced to dryness under reduced pressure. The yellow-solids were extracted with pentane, leaving a white powder. Concentration of the pentane solution gave yellow microcrystals which were determined to be a mixture of **1** (10%) and **4**. Further recrystallizations of the product from pentane gave 0.163 g (0.252 mmol, 40.5% yield) of **4**. ¹H NMR: δ 13.14 (s, 1H, CHC(CH₃)₂Ph); 8.24, 7.62, 7.32, 7.30, 7.28, 6.99 (each as d, 1 H each, Tp ring protons, 3,5-positions); 7.4 - 6.8 (m, 8 H, Ph, Ar); 5.90, 5.71, 5.64 (each a t, 1 H each, Tp ring protons, 4-position); 4.82, 3.42 (br m, 1 H each, CH(CH₃)₂); 4.60 (s, 3H, OCH₃); 2.02, 1.79 (each a s, 3H each, CHC(CH₃)₂Ph); 1.59, 1.00, 0.14 (each as br d, 6:3:3 H, CH(CH₃)₂). ¹³C NMR: δ

302.2 ($^1J_{\text{CH}} = 121$ Hz, $\text{CHC}(\text{CH}_3)_2\text{Ph}$, 151.3, 150.6, 146.6, 141.2, 139.9, 135.5, 134.4, 133.8, 128.6, 127.3, 127.0, 126.6, 125.8, 123.9, 123.0, 105.4, 105.0, 104.8, 72.7 (OCH_3 , $^1J_{\text{CH}} = 137.3$ Hz), 53.7, 33.1, 31.5, 28.2, 27.4, 25.7, 24.3, 23.0. Elemental analysis calculated for $\text{C}_{32}\text{H}_{42}\text{BMoN}_7\text{O}$: C, 59.36; H, 6.54; N, 15.14. Found: C, 59.36; H, 6.58; N, 15.13. IR: $\nu_{\text{OMe}} = 2778.2$ cm^{-1} , $\nu_{\text{BH}} = 2472.6$ cm^{-1} , $\nu_{\text{OMe}} = 1081.8$ cm^{-1} .

$\text{TpMo}(\text{CC}(\text{CH}_3)_2\text{Ph})(\text{NHAr})(\text{OCH}_3)$ (**5**)

Compound **1** (0.664 g, 0.867 mmol) and an excess of potassium methoxide (.300 g, 4.28 mmol) were dissolved in THF at -78°C to give a yellow slurry. The mixture was allowed to warm to room temperature and stirring continued for 24 hours. The solution became red-orange and the white solids remained. The THF was removed under reduced pressure and the residue was extracted with Et_2O . Concentration of the Et_2O extract and cooling to -20°C gave orange crystals of the product **5**. Two further crops of crystals were obtained to give a combined yield of 78 %. (0.439 g, 0.678 mmol). ^1H NMR of major rotamer (CD_2Cl_2 , -40.0°C): δ 9.55 (br s, 1 H, NH), 8.06, 7.72, 7.71, 7.69, 7.60, 6.19 (each as d, 1 H each, Tp ring protons, 3,5-positions); 7.38, 7.19, 7.09 (t:d:d, 1:1:1 H, Ar ring protons); 6.61, 7.01, 5.98 (d:t:t, 2:2:1 H, Ph ring protons); 6.30, 6.24, 5.81 (each a t, 1 H each, Tp ring protons, 4-position); 5.11 (s, 3H, OCH_3); 4.79, 2.13 (sept, 1 H each, $\text{CH}(\text{CH}_3)_2$); 4.52 (br s, 1 H, HB), 1.49, 1.38 (each a s, 3H each, $\text{CHC}(\text{CH}_3)_2\text{Ph}$); 1.56, 1.20, 0.96, 0.60 (each a d, 3 H each, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR: δ 301.3, 155.2, 145.2, 144.9, 142.6, 142.4, 139.7, 139.3, 135.4, 135.0, 134.9, 128.3, 126.2, 125.8, 123.8, 123.2, 121.8, 105.5, 105.1, 103.9, 73.7, 57.6, 30.8, 28.0, 27.0, 26.4, 24.7, 24.0, 21.5, 21.0. Elemental analysis calculated for $\text{C}_{32}\text{H}_{42}\text{BMoN}_7\text{O}$: C, 59.36; H, 6.54; N, 15.14. Found: C, 59.30; H, 6.57; N, 15.11. IR: $\nu_{\text{NH}} = 3308.7$ cm^{-1} , $\nu_{\text{OMe}} = 2781$ cm^{-1} , $\nu_{\text{BH}} = 2472.9$ cm^{-1} , $\nu_{\text{OMe}} = 1083.9$ cm^{-1} . ^1H NMR of minor rotamer (CD_2Cl_2 , -40.0°C): δ 10.26 (br s, 1 H, NH), 8.08, 7.76, 7.66, 7.54, 7.45, 6.63 (each as d, 1 H each, Tp ring

protons, 3,5-positions); 6.29, 6.23, 5.66 (each a t, 1 H each, Tp ring protons, 4-position); 4.98 (s, 3H, OCH₃); 3.68, 2.90 (sept, 1 H each, CH(CH₃)₂); 1.73, 1.53 (each a s, 3H each, CHC(CH₃)₂Ph); 1.31, 0.96, 0.44, -0.28 (each a d, 3 H each, CH(CH₃)₂). Ar and Ph protons of minor isomer not discernible. ¹³C NMR: δ 298.7, 149.0, 145.4, 144.8, 144.7, 142.0, 141.4, 135.6, 134.4, 133.8, 129.0, 126.4, 126.0, 124.8, 122.6, 122.2, 122.1, 105.2, 103.8, 72.4, 57.4, 31.1, 27.7, 26.7, 25.3, 24.1, 22.7, 22.2, 20.0.

TpMo(CHC(CH₃)₂Ph)(NAr)(CH₃) (6)

To a stirring solution of **1** (0.39 g, 0.51 mmol) in 50 mL Et₂O, was added an ether solution of CH₃Li (0.6 mL, 1.4M, 0.84 mmol) at room temperature under argon. A yellowish brown solution resulted after 3 hours, and the solvent was removed under reduced pressure. The residue was extracted with pentane (2 x 10 mL), and the combined extracts were passed through Celite. Removal of the solvent yielded oily, yellowish brown solids. Extracting the solids in Et₂O and filtering through a column of neutral alumina resulted in a yellow solution. Removal of the solvent gave the product as a yellow solid (0.24 g, 0.38 mmol, 74.5 % yield). The product can be recrystallized from Et₂O. ¹H NMR data (300 MHz, C₆D₆, 22 °C): δ 13.11 (s, 1H, CHC(CH₃)₂Ph); 8.00, 7.62, 7.45, 7.36, 7.32, 7.23 (each as d, 1 H each, Tp ring H's, 3,5-positions); 7.54 (d, 2 H, ortho H's of neophylidene phenyl); 7.25 (t, 2 H, meta H's of neophylidene phenyl); 7.12 - 6.85 (m, 4 H, para H of neophylidene phenyl, meta and para H's of aryl imido); 5.78, 5.76, 5.74 (each a t, 1 H each, Tp ring H's, 4-position); 4.54, 3.28 (each a broad sept, 1 H each, CH(CH₃)₂); 1.95, 1.78, 1.29 (each a s, 3 H each, CHC(CH₃)₂Ph, CH₃); 1.42, 1.02, 0.29 (each a broad d, 6:3:3 H, CH(CH₃)₂). ¹³C NMR data (75 MHz, C₆D₆, 22 °C): δ 302.5 (¹J_{CH} = 115 Hz, CHC(CH₃)₂Ph); 148.4, 146.8, 142.3, 142.1, 135.5, 134.4, 127.0, 126.5, 125.8, 124.0, 123.3, 105.9, 105.2 (Tp, Ph, Ar); 53.7 (CHC(CH₃)₂Ph); 32.0, 30.9, 27.9, 26.7, 24.0, 23.7, 22.9, (CH(CH₃)₂, CHC(CH₃)₂Ph); 18.0 (¹J_{CH} = 123 Hz, CH₃). Elemental analysis calculated for

$C_{32}H_{42}BMoN_7$: C, 60.86; H, 6.70; N, 15.53. Found: C, 60.94; H, 6.87; N, 15.55. IR: $\nu_{BH} = 2484\text{ cm}^{-1}$

Reaction of $TpMo(CHC(CH_3)_2Ph)(NAr)(CH_3)$ (**6**) with HOTf

Compound **2** (0.023 g, 0.036 mmol) was dissolved in C_6D_6 in an NMR tube under nitrogen. HOTf (3.3 μ L, 0.037 mmol) was added by syringe. After 10 minutes, a 1H NMR spectrum of the reaction mixture showed that **6** was completely converted to **1**. The formation of CH_4 was observed as a singlet at δ 0.20.

$[TpMo(CHC(CH_3)_2Ph)(NAr)(Et_2O)][BAr'_4]$ (**7**)

A 10 mL Et_2O solution of $HBAr'_4 \cdot 2 Et_2O$ (0.16 g, 0.16 mmol) and a 10 mL ethereal solution of **6** (0.10 g, 0.16 mmol) were each cooled to $-78\text{ }^\circ\text{C}$. The two solutions were mixed and stirred for 12 h under argon at $-78\text{ }^\circ\text{C}$. The solvent was removed under reduced pressure at $-78\text{ }^\circ\text{C}$, the brown solids were washed with pentane at $-78\text{ }^\circ\text{C}$. The residual product was dried under reduced pressure to give oily brown solids. 1H NMR data for **3** (CD_2Cl_2 , 22°C): δ 14.79 (s, 1 H, $\underline{CHC}(CH_3)_2Ph$); 8.28, 7.89, 7.82, 7.77, 7.48, 6.62 (each a d, 1 H each, Tp ring H's, 3,5-positions); 7.83 (s, 8 H, *o*-Ar'); 7.64 (s, 4 H, *p*-Ar'); 7.60 - 7.18 (m, 8 H, Ph, Ar); 6.51, 6.28, 6.12 (t, 1 H each, Tp ring H's, 4-position); 3.93, 3.60 (each a ABX₃ m, 2 H each, $O(\underline{CH_2CH_3})_2$); 4.03, 2.50 (each a broad sept, 1 H each, $\underline{CH}(CH_3)_2$); 2.01, 1.99 (each a s, 3 H each, $CHC(\underline{CH_3})_2Ph$); 1.62, 1.48, 0.92, -0.08 (each a broad d, 3 H each, $CH(\underline{CH_3})_2$); 0.89 (t, 6 H, $O(CH_2\underline{CH_3})_2$). ^{13}C NMR data for **7** (CD_2Cl_2 , 22°C): δ 337.4 ($\underline{CHC}(CH_3)_2Ph$); 162.2 ($^1J_{BC} = 50\text{ Hz}$, ipso-Ar' carbon); 153.0-107.0 (23 resonances, Ph, Ar', Tp); 125.2 ($^1J_{FC} = 270\text{ Hz}$, CF_3); 76.9 ($O(\underline{CH_2CH_3})_2$); 30.8, 30.6 ($CHC(\underline{CH_3})_2Ph$); 28.8, 28.6 ($\underline{CH}(CH_3)_2$); 25.2, 25.0, 23.4, 22.6 ($CH(\underline{CH_3})_2$); 12.5 ($O(CH_2\underline{CH_3})_2$).

[TpMo(CHC(CH₃)₂Ph)(NAr)(NCCH₃)] [B(C₆F₅)₄] (8)

Compound **6** (0.331 g, 0.524 mmol) and trityl tetrakis(pentafluorophenyl)borate (0.515 g, 0.558 mmol) were dissolved separately in Et₂O at -78 °C and mixed to give a yellow solution. The solution was stirred and allowed to warm to room temperature over 30 minutes to give a yellow-brown solution. 5 mL of acetonitrile was transferred to the reaction and the mixture was re-cooled to -78 °C and stirred for one hour. The solvent was removed under reduced pressure and the oily brown residue was washed with pentane. Attempts to recrystallize the product from Et₂O were unsuccessful, but evaporation of an ethereal solution results in an analytically pure solid. The yield is essentially quantitative. ¹H NMR for major rotamer (CD₂Cl₂, -40.0 °C): δ 14.47 (s, 1H, CHC(CH₃)₂Ph); 7.94, 7.88, 7.82, 7.80, 7.73, 6.94 (each as d, 1 H each, Tp ring protons, 3,5-positions); 7.38 - 7.09 (m, 8 H, Ph, Ar); 6.36, 6.27, 6.20 (each a t, 1 H each, Tp ring protons, 4-position); 3.96, 2.40 (sept, 1 H each, CH(CH₃)₂); 2.35 (s, 3H, NCCH₃); 1.89, 1.81 (each a s, 3H each, CHC(CH₃)₂Ph); 1.49, 1.30, 0.81, -0.02 (each a d, 3 H each, CH₂(CH₃)₂). ¹³C NMR: δ 340.6 (¹J_{CH} = 124.3 Hz), 148.6, 138.6, 136.7 (br d, ¹J_{CF} = 244.4-238.8 Hz), 149.7, 148.2, 148.0, 146.4, 142.2, 142.1, 141.7, 138.8, 137.1, 136.7, 135.5, 130.5, 129.2, 127.3, 126.5, 124.6, 107.2, 106.8, 106.7, 57.9, 30.1, 29.6, 29.1, 28.4, 26.3, 23.8, 23.4, 22.3, 4.0. Elemental analysis calculated for C₅₇H₄₂B₂F₂₀MoN₈: C, 51.22; H, 3.17; N, 8.38. Found: C, 50.81; H, 2.95; N, 7.69. ¹H NMR for minor rotamer (CD₂Cl₂, -40.0 °C): δ 15.28 (s, 1H, CHC(CH₃)₂Ph); 7.98, 7.65, 7.52, 7.30, 7.03, 6.01 (each as d, 1 H each, Tp ring protons, 3,5-positions); 6.45, 6.20, 6.07 (each a t, 1 H each, Tp ring protons, 4-position); 2.32 (s, 3H, NCCH₃); 1.93, 1.87 (each a s, 3H each, CHC(CH₃)₂Ph); Ar, Ph, and *i*-Pr resonances are not distinguishable in the spectrum..

[TpMo(CHC(CH₃)₂Ph)(NAr)(NCCH₃)] [B(CH₃)(C₆F₅)₃] (9)

Compound **6** (0.153 g, 0.242 mmol) and tris(pentafluorophenyl)boron (0.124 g, 0.242 mmol) were dissolved separately in Et₂O at -78 °C and allowed to warm to room

temperature over 30 minutes to give a yellow-brown solution. 5 mL of acetonitrile was transferred to the reaction and the mixture was recooled to -78 °C and stirred for one hour. The solvent was removed under reduced pressure and the oily brown residue was washed with pentane. Attempts to recrystallize the product from Et₂O were unsuccessful, but evaporation of an ethereal solution results in an analytically pure solid. The yield is essentially quantitative. ¹H NMR for major rotamer (CD₂Cl₂, 22 °C): δ 14.53 (s, 1H, CHC(CH₃)₂Ph); 7.94, 7.90, 7.84, 7.82, 7.33, 7.12 (each as d, 1 H each, Tp ring protons, 3,5-positions); 7.40 - 7.07 (m, 8 H, Ph, Ar); 6.41, 6.34, 6.32 (each a t, 1 H each, Tp ring protons, 4-position); 3.98, 2.46 (sept, 1 H each, CH(CH₃)₂); 2.34 (s, 3H, NCCH₃); 1.97, 1.81 (each a s, 3H each, CHC(CH₃)₂Ph); 1.52, 1.35, 0.87, 0.08 (each a d, 3 H each, CH(CH₃)₂) 0.47 (br s, 3 H, BCH₃). ¹³C NMR: δ 340.9 (¹J_{CH} = 125.9 Hz), 148.6, 138.6, 136.7 (br d, ¹J_{CF} = 244.4-238.8 Hz), 149.6, 148.1, 148.0, 146.3, 142.13, 142.07, 141.7, 138.8, 137.0, 136.7, 135.4, 130.5, 129.2, 128.8, 127.3, 126.4, 124.6, 107.2, 106.8, 58.0, 30.1, 29.8, 29.1, 28.4, 26.3, 25.2, 23.8, 23.4, 22.3, 4.2. Elemental analysis calculated for C₅₂H₄₅B₂F₁₅MoN₈: C, 52.73; H, 3.83; N, 9.46. Found: C, 53.09; H, 3.59; N, 9.14.

[TpMo(CHC(CH₃)₂Ph)(NAr)(THF)][B(CH₃)(C₆F₅)₃] (10)

Compound 6 (0.084 g, 0.133 mmol) and tris(pentafluorophenyl)boron (0.068 g, 0.134 mmol) were dissolved separately in Et₂O at -78 °C and allowed to warm to room temperature over 30 minutes to give a yellow-brown solution. 5 mL of THF was transferred to the reaction and the mixture was recooled to -78 °C and stirred for one hour. The solvent was removed under reduced pressure and the oily brown residue was washed with pentane. Attempts to recrystallize the product from Et₂O were unsuccessful, but evaporation of an ethereal solution results in an analytically pure solid. The yield is essentially quantitative. ¹H NMR for major rotamer (CD₂Cl₂, 22 °C): δ 14.46 (s, 1H, CHC(CH₃)₂Ph); 8.00, 7.90, 7.85, 7.78, 6.46 (each as d, 1 H each, Tp ring protons, 3,5-

positions); 7.46 - 7.04 (m, 9 H, Ph, Ar, one Tp ring proton); 6.51, 6.23, 6.11 (each a t, 1 H each, Tp ring protons, 4-position); 3.81, 2.48 (sept, 1 H each, $\text{CH}(\text{CH}_3)_2$); 3.65, 3.55, 1.82 (t:t:t, 2:2:4, THF); 1.98, 1.91 (each a s, 3H each, $\text{CHC}(\text{CH}_3)_2\text{Ph}$); 1.58, 1.39, 0.94, -0.12 (each a d, 3 H each, $\text{CH}(\text{CH}_3)_2$) 0.47 (br s, 3 H, BCH_3). ^{13}C NMR: δ 336.4, 148.8, 138.6, 136.7 (three br d, $^1\text{J}_{\text{CF}} = 244\text{-}240$ Hz), 148.4, 146.2, 144.2, 142.6, 140.5, 138.8, 137.4, 136.2, 133.6, 129.6, 128.2, 126.6, 125.7, 124.6, 123.6, 107.9, 107.5, 107.1, 106.9, 106.3, 82.9, 57.5, 31.8, 30.7, 30.3, 28.9, 28.4, 26.9, 25.9, 25.4, 24.4, 22.7. Elemental analysis calculated for $\text{C}_{54}\text{H}_{50}\text{B}_2\text{F}_{15}\text{MoN}_7\text{O}$: C, 53.36; H, 4.15; N, 8.07. Found: C, 52.95; H, 4.26; N, 7.81.

[TpMo(CHC(CH₃)₂Ph)(NAr)(P(CH₃)₃)](OSO₂CF₃) (11)

0.5 mL of a 0.17M $\text{P}(\text{CH}_3)_3$ solution in C_6D_6 (0.085 mmol $\text{P}(\text{CH}_3)_3$) was added to **1** (0.032 g, 0.042 mmol) in a sealable NMR tube. Pale yellow solids formed over 2 hours, and the C_6D_6 was removed under reduced pressure and the resulting solids were dissolved in CD_2Cl_2 . The yield was quantitative by ^1H NMR. ^1H NMR for major rotamer (CD_2Cl_2 , -20 °C): δ 14.51 (d, 1H, $\text{CHC}(\text{CH}_3)_2\text{Ph}$, $^3\text{J}_{\text{PH}} = 5.4$ Hz); 8.23, 7.99, 7.88, 7.85, 7.38, 7.28 (each as d, 1 H each, Tp ring protons, 3,5-positions); 7.45 - 7.06 (m, 8 H, Ph, Ar); 6.48, 6.38, 6.25 (each a t, 1 H each, Tp ring protons, 4-position); 3.74, 2.23 (sept, 1 H each, $\text{CH}(\text{CH}_3)_2$); 2.03, 1.86 (each a s, 3H each, $\text{CHC}(\text{CH}_3)_2\text{Ph}$); 1.60, 1.42, 0.59, 0.31 (each a br d, 3 H each, $\text{CH}(\text{CH}_3)_2$); 1.12 (d, 9H, $\text{P}(\text{CH}_3)_3$, $^2\text{J}_{\text{PH}} = 9.9$ Hz). ^{13}C NMR (CD_2Cl_2 , 22 °C): δ 335.9 ($^1\text{J}_{\text{CH}} = 122.1$ Hz, $^2\text{J}_{\text{PC}} = 17.6$ Hz), 147.7, 147.2, 143.9, 143.1, 138.2, 137.9, 137.8, 130.2, 129.4, 127.3, 126.2, 125.0, 123.7, 119.4, 107.9, 107.1, 107.0, 57.0, 31.6, 30.2, 28.3, 26.2, 24.9, 17.6 ($^1\text{J}_{\text{PC}} = 30.2$ Hz). ^{19}F NMR (282 MHz, vs. CFCl_3): δ -78.75. ^{31}P NMR (121 MHz, vs. H_3PO_4): δ -2.83. Elemental analysis calculated for $\text{C}_{35}\text{H}_{48}\text{BF}_3\text{MoN}_7\text{O}_3\text{PS}$: C, 49.95; H, 5.75; N, 11.65. Found: C, 49.58; H, 5.68; N, 11.25. IR (CD_2Cl_2 film): 1268, 1048 cm^{-1} (S=O).

Preparation of $[(\text{H}_3\text{CO})_2\text{C}_6\text{H}_2(\text{NSi}(\text{CH}_3)_3)_2]\text{W}(\text{NPh})(\text{Cl})_2$, **17**

Trimethylsilyl chloride (11.7 mL, 92.2 mmol) was added slowly to a slurry of 4,5-diaminoveratrole (7.38 g, 43.9 mol) in 250 mL of Et_2O . The slurry thickened upon addition. Triethylamine (12.8 mL, 91.8 mmol) was added slowly, and the slurry was stirred for three hours at room temperature. The mixture was filtered giving a yellow filtrate, and the off-white solids were washed twice with 20 mL portions of Et_2O . The solvent was removed from the filtrate under reduced pressure to give $(\text{H}_3\text{CO})_2\text{C}_6\text{H}_2(\text{NHSi}(\text{CH}_3)_3)_2$ (10.8 g, 34.6 mmol, 78.8 % yield) as a light yellow solid. ^1H NMR (CDCl_3 , 20 °C): δ 6.46 (s, 2H, ring protons); 3.80 (s, 6H, OCH_3); 2.96 (br s, 2H, NH); 0.21 (s, 18H, $\text{Si}(\text{CH}_3)_3$). ^{13}C NMR: δ 143.2, 130.9, 106.9, 56.7, 0.4. M.P. 52 °C.

$(\text{H}_3\text{CO})_2\text{C}_6\text{H}_2(\text{NHSi}(\text{CH}_3)_3)_2$ (3.13 g, 10.01 mmol) was dissolved in 50 mL of Et_2O and cooled to -78 °C. Two equivalents of $n\text{-BuLi}$ (8 mL, 20 mmol, 2.5 M in hexanes) was slowly added, and an off-white precipitate formed. This slurry was allowed to warm to ambient temperature and was stirred for one hour. A gas was evolved upon warming. This slurry was cooled to -78 °C and added to a stirring green solution of $\text{W}(\text{NPh})(\text{Cl})_4(\text{Et}_2\text{O})$ (4.58 g, 9.29 mmol, 0.93 equivalents) in Et_2O at -78 °C. The solution turned dark red to dark brown during addition and upon warming to room temperature and stirring for three hours. The resulting dark brown solution was filtered through Celite, and the brown solids were washed liberally with additional portions of Et_2O . The combined Et_2O filtrates were stripped of solvent under reduced pressure. The dark solids were washed with two 10 mL portions of pentane, and the pentane washes were concentrated and cooled giving **17**. ^1H NMR (C_6D_6 , 20 °C): δ 7.37 (d, 2 H, NPh); 7.04 (t, 2 H, NPh); 6.75 (t, 1 H, NPh); 6.56 (s, 2H, ring protons); 3.28 (s, 6H, OCH_3); 0.23 (s, 18H, $\text{Si}(\text{CH}_3)_3$). ^1H NMR (CD_2Cl_2 , 20 °C): δ 7.46 (t, 2 H, NPh); 7.27 (d, 2 H, NPh); 7.19 (t, 1 H, NPh); 6.73 (s, 2H, ring protons); 3.96 (s, 6H, OCH_3); 0.46 (s, 18H,

$\text{Si}(\text{CH}_3)_3$). ^{13}C NMR (CD_2Cl_2 , 20 °C): δ 155.0, 153.2, 128.8, 128.2, 126.3, 123.1, 101.9, 56.3, 0.8.

Preparation of $[(\text{H}_3\text{CO})_2\text{C}_6\text{H}_2(\text{NSi}(\text{CH}_3)_3)_2]\text{W}(\text{NPh})(\text{Cl})_2(\text{P}(\text{CH}_3)_3)$, **19**

Compound **17** (0.516 g, 0.786 mmol) was dissolved in 30 mL of Et_2O at room temperature to give a dark red-brown solution. Trimethylphosphine (0.22 mL, 2.13 mmol) was added by syringe to immediately give a blue-violet solution which was stirred for 10 minutes. The solvent and excess phosphine were removed under reduced pressure to give 0.552 g of a dark blue powder, **19**. ^1H NMR indicated that conversion to the phosphine adduct was quantitative (96 % yield) ^1H NMR (C_6D_6 , 20 °C): δ 7.58 (d, 2 H, NPh); 7.19 (t, 2 H, NPh); 6.67 (t, 1 H, NPh); 6.67 (s, 2H, ring protons); 3.46 (s, 6H, OCH_3); 0.85 (d, 9 H, $\text{P}(\text{CH}_3)_3$, $^2J_{\text{PH}} = 7.8$ Hz); 0.49 (s, 18H, $\text{Si}(\text{CH}_3)_3$). ^1H NMR (CD_2Cl_2 , 20 °C): δ 7.48 (t, 2 H, NPh); 7.24 (d, 2 H, NPh); 7.03 (t, 1 H, NPh); 6.69 (s, 2H, ring protons); 3.94 (s, 6H, OCH_3); 0.91 (d, 9 H, $\text{P}(\text{CH}_3)_3$, $^2J_{\text{PH}} = 8.1$ Hz); 0.38 (s, 18H, $\text{Si}(\text{CH}_3)_3$). ^{13}C NMR (CD_2Cl_2 , 20 °C): δ 153.2, 148.5, 138.0, 129.3, 128.1, 127.9, 126.8, 126.5, 103.2, 56.3, 12.4, 1.78.

Crystallographic Studies

X-ray data collection and structure refinement for compounds **2** and **3**.

Compound **2**: $\text{C}_{31}\text{H}_{40}\text{BN}_7\text{OMo}$, $M_r = 633.45$, Triclinic, $P\bar{1}$, $a = 9.419(1)$ Å, $b = 12.816(1)$ Å, $c = 14.698(2)$ Å, $\alpha = 100.73(1)^\circ$, $\beta = 94.71(1)^\circ$, $\gamma = 108.89(1)^\circ$, $V = 1629.5(3)$ Å³, $Z = 2$, $D_{\text{calc.}} = 1.291$ g cm⁻³, Mo K_α ($\lambda = 0.71073$ Å), $T = 298$ K.

Compound **3**: $\text{C}_{42}\text{H}_{54}\text{B}_2\text{N}_{14}\text{O}_3\text{Mo}_2$, $M_r = 1016.49$, Monoclinic, $P2_1/n$, $a = 11.419(4)$ Å, $b = 17.597(5)$ Å, $c = 12.320(4)$ Å, $\beta = 98.16(3)^\circ$, $V = 2451(1)$ Å³, $Z = 2$, $D_{\text{calc.}} = 1.378$ g cm⁻³, Mo K_α ($\lambda = 0.71073$ Å), $T = 298$ K. Data were collected at room temperature on a Siemens R3m/V diffractometer equipped with a graphite monochromator utilizing Mo K_α

radiation ($\lambda = 0.71073 \text{ \AA}$). 32 reflections from each structure with $20.0^\circ \leq 2\theta \leq 22.0^\circ$ were used to refine the cell parameters. 7953 and 3402 reflections, for **2** and **3** respectively, were collected using the ω -scan method (**2**: 2θ range $3\text{--}55^\circ$, 1.2° scan range and $4\text{--}8^\circ$ scan speed depending on intensity; **3**: 2θ range $3\text{--}45^\circ$, 1.2° scan range and $3\text{--}6^\circ$ scan speed depending on intensity). Four reflections (110 , $12\bar{2}$, $02\bar{1}$, $\bar{1}12$) for **2**, and ($02\bar{2}$), $1\bar{1}0$, 120 , $10\bar{1}$) for **3**, were measured every 96 reflections to monitor instrument and crystal stability (maximum corrections on I were 2 %, respectively). Absorption corrections were applied based on measured crystal faces using *SHELXTL plus*.¹²¹ Absorption coefficients: **2**, $\mu = 0.44 \text{ mm}^{-1}$ (min. and max. transmission factors are 0.882 and 0.904, respectively); **3**, $\mu = 0.56 \text{ mm}^{-1}$ (min. and max. transmission factors are 0.940 and 0.958, respectively).

The structures were solved by the heavy atom method in *SHELXTL plus* from which the positions of the Mo atoms were obtained. The rest of the non-H atoms were obtained from subsequent Difference Fourier maps. The structures were refined in *SHELXTL plus* using full-matrix least squares. All of the non-H atoms were refined with anisotropic thermal parameters. All of the non-methyl H atoms in **2** were located from a Difference Fourier map and were refined without any constraints. The methyl H atoms were calculated in idealized positions and their thermal parameters were fixed. In **3**, all of the H atoms were calculated in idealized positions and their thermal parameters were fixed. The boron H atom was located from a Difference Fourier map and was refined without any constraints. 530 and 299 parameters for **2** and **3**, respectively, were refined and $\sum w(|F_o| - |F_c|)^2$ was minimized; $w = 1/(\sigma|F_o|)^2$, $\sigma(F_o) = 0.5 \text{ kI}^{-1/2}\{[\sigma(I)]^2 + (0.02I)^2\}^{1/2}$, $I(\text{intensity}) = (I_{\text{peak}} - I_{\text{background}})(\text{scan rate})$, and $\sigma(I) = (I_{\text{peak}} + I_{\text{background}})^{1/2}(\text{scan rate})$, k is the correction due to decay and L_p effects, 0.02 is a factor used to down weight intense reflections and to account for instrument instability. $R = 0.0323$ and $wR = 0.0411$ for **2**, and $R = 0.0619$ and $wR = 0.063$ for **3**, in the last cycle of refinement using 6765 and 1738 reflections [with $I > 2\sigma(I)$], for **2** and **3**, respectively. The linear

absorption coefficient was calculated from values from the *International Tables for X-ray Crystallography*.¹²² The final atomic coordinates for the non-hydrogen of compounds **2** and **3** are given in Appendix A. Scattering factors for non-hydrogen atoms were taken from Cromer & Mann¹²³ with anomalous-dispersion corrections from Cromer & Liberman,¹²⁴ while those of hydrogen atoms were from Stewart, Davidson & Simpson.

X-ray data collection and structure refinement for compounds **4** and **5**

Compound **4**: $C_{32}H_{42}BN_7OMo$, $M_r = 647.48$, Orthorhombic, $P2_12_12_1$, $a = 12.620(2) \text{ \AA}$, $b = 13.492(2) \text{ \AA}$, $c = 19.682(2) \text{ \AA}$, $V = 3351.3(7) \text{ \AA}^3$, $Z = 4$, $D_{calc.} = 1.283 \text{ g cm}^{-3}$, Mo K_{α} ($\lambda = 0.71073 \text{ \AA}$), $T = 298 \text{ K}$. Compound **5**: $C_{32}H_{42}BN_7OMo$, $M_r = 647.48$, Triclinic, $P\bar{1}$, $a = 10.624(2) \text{ \AA}$, $b = 11.766(3) \text{ \AA}$, $c = 13.980(3) \text{ \AA}$, $\alpha = 86.96(2)^\circ$, $\beta = 86.54(2)^\circ$, $\gamma = 67.77(2)^\circ$, $V = 1635.8(7) \text{ \AA}^3$, $Z = 2$, $D_{calc.} = 1.315 \text{ g cm}^{-3}$, Mo K_{α} ($\lambda = 0.71073 \text{ \AA}$), $T = 298 \text{ K}$. Data were collected at room temperature on a Siemens R3m/V diffractometer equipped with a graphite monochromator utilizing Mo K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$). 32 reflections from each structure with $20.0^\circ \leq 2\theta \leq 22.0^\circ$ were used to refine the cell parameters. 4317 and 6094 reflections, for **4** and **5** respectively, were collected using the ω -scan method (**4**: 2θ range $3\text{--}55^\circ$, 1.2° scan range and $3\text{--}6^\circ$ scan speed depending on intensity; **5**: 2θ range $3\text{--}50^\circ$, 1.2° scan range and $3\text{--}6^\circ$ scan speed depending on intensity). Four reflections from each data, were measured every 96 reflections to monitor instrument and crystal stability (maximum corrections on I were $< 1 \%$, and 4% , respectively). Absorption corrections were applied based on measured crystal faces using *SHELXTL plus*.¹²¹ Absorption coefficients: **4**, $\mu = 0.43 \text{ mm}^{-1}$ (min. and max. transmission factors are 0.928 and 0.950, respectively); **5**, $\mu = 0.44 \text{ mm}^{-1}$ (min. and max. transmission factors are 0.850 and 0.948, respectively).

The structures were solved by the heavy atom method in *SHELXTL plus* from which the positions of the Mo atoms were obtained. The rest of the non-H atoms were obtained from subsequent Difference Fourier maps. The structures were refined in

SHELXTL plus using full-matrix least squares. In **4**: The alkylidene ligand was found to be disordered by a 20° rotation around the C1-C4 bond. The site occupation value for one partial moiety was refined to 0.69(1); thus the other part of the disordered moiety had a site occupation value of 0.31(1). All of the non-H atoms were refined with anisotropic thermal parameters except the disordered atoms (C2, C3, C5-to-C10 and C2', C3', C5'-to-C10'). All of the H atoms were calculated in idealized positions and their thermal parameters were fixed (The Boron H atom was located from a Difference Fourier map and was refined without any constraints). In **5**, all of the non-H atoms were refined with anisotropic thermal parameters. The H atoms were calculated in idealized positions and their thermal parameters were fixed; The Boron H atom was located from a Difference Fourier map and was refined without any constraints. 352 and 463 parameters for **4** and **5**, respectively, were refined and $\sum w (|F_o| - |F_c|)^2$ was minimized; $w=1/(\sigma |F_o|)^2$, $\sigma(F_o) = 0.5 kI^{-1/2} \{ [\sigma(I)]^2 + (0.02I)^2 \}^{1/2}$, $I(\text{intensity}) = (I_{\text{peak}} - I_{\text{background}})(\text{scan rate})$, and $\sigma(I) = (I_{\text{peak}} + I_{\text{background}})^{1/2}(\text{scan rate})$, k is the correction due to decay and L_p effects, 0.02 is a factor used to down weight intense reflections and to account for instrument instability. $R = 0.0600$ and $wR = 0.0589$ for **4**, and $R = 0.0484$ and $wR = 0.0487$ for **5**, in the last cycle of refinement using 2298[with $I > 3\sigma(I)$] and 4596[with $I > 2\sigma(I)$] reflections, for **4** and **5**, respectively. Fractional coordinates for the atoms of compounds **4** and **5** are given in the appendix tables A.20 and A.25, respectively.

X-ray Data Collection and Refinement for Complex 16

The dark brown crystals are air sensitive and were crystallized in an inert atmosphere. In previous attempts, crystals mounted in glass capillaries decomposed in less than 24 hours. The data crystal was mounted in a glass capillary and data collection proceeded at a faster than usual speed (15-30 deg./min., depending on intensity) in order to collect an entire unique data set in less than a 24 hour time. The crystal started decaying significantly after the end of data collection. Data were collected at room temperature on a

Siemens P3m/V diffractometer equipped with a graphite monochromator utilizing $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). 25 reflections with $4^\circ \leq 2\theta \leq 20^\circ$ were used to refine the cell parameters. Four reflections were measured every 96 reflections to monitor instrument and crystal stability (maximum corrections on I was 10 %). Absorption corrections were not applied.

The structure was solved by the heavy-atom method in *SHELXTL plus*¹ from which the location of the W atom was obtained. The rest of the non-hydrogen atoms were obtained from a subsequent Difference Fourier map. The structure was refined in *SHELXTL plus*¹²¹ using full-matrix least squares and all of the non-H atoms were refined anisotropically. The H-atoms were calculated in ideal positions (C-H bond, 0.96 $\text{\AA}$) and their isotropic thermal parameters were fixed. The linear absorption coefficients were calculated from values from the *International Tables for X-ray Crystallography*.¹²² Scattering factors for non-hydrogen atoms were taken from Cromer & Mann¹²³ with anomalous-dispersion corrections from Cromer & Liberman,¹²⁴ while those of hydrogen atoms were from Stewart, Davidson & Simpson.

Alkylidene Rotational Studies

Determination of Activation Parameters for the Thermal Isomerization of the *Anti* to the *Syn* Rotamer of **1**

An nOe difference study of the major isomer of **1** indicated it to be the *syn* rotamer. Irradiation of the alkylidene proton showed 0% enhancement of the methine proton of the isopropyl groups. Irradiation of the methyl groups of the alkylidene ligand caused a 8.7% enhancement of the methine protons. To determine the rotational rates of conversion for the minor *anti* rotamer to the major *syn* rotamer, 0.02 g of **1** was dissolved in approximately 1 mL dg-toluene and sealed in an NMR tube. The NMR tube was placed in a Pyrex beaker containing dry ice/isopropanol as a coolant and irradiated by a 275 watt

tungsten lamp for 1 h to give *syn:anti* rotamer ratio of approximately 4:1. A temperature of -50 °C was typically employed. The alkylidene proton signal for the minor isomer is δ 14.82. The thermal isomerization of the *anti* to the *syn* rotamer was followed by ^1H NMR at 40.0, 50.0, and 60.0 °C by integration of the alkylidene resonances for a minimum of 3 half lives. Rates were also determined by this method for **2** and **8**. Decomposition of **1** was determined to be less than 1% by summing the integration of the *syn* and *anti* rotamers over time. The rate constants k were determined by plotting the $\ln$ of the integral of the *anti* rotamer versus time. The rate constants were $8.2 \pm 0.1 \times 10^{-5}$, $2.4 \pm 0.1 \times 10^{-4}$, and $7.0 \pm 0.1 \times 10^{-4} \text{ sec}^{-1}$ for 40.0, 50.0, and 60.0 °C, respectively. A $\Delta H^\ddagger$ of $+21.5 \pm 0.3$ kcal/mole and a $\Delta S^\ddagger$ of -8.9 ± 0.8 e.u. were determined from a plot of $\ln(k/T)$ vs. $(1/T)$.

Polymerizations

ROMP reactions by **1** and **6** with AlCl_3

In a typical reaction, recrystallized **1** or **6** was dissolved in 500 equivalents of neat cyclooctene or norbornylene. An excess of AlCl_3 (6 equivalents) was added, and a red solution immediately formed. The solution became viscous and stirring ceased within 10 minutes. The polymer was dissolved in 10 mL toluene, and the viscosity increased over 24 hours. The polymer was precipitated in methanol with 20 mg BHT (3 times), filtered, and dried under reduced pressure to yield a white solid. Molecular weights were determined by GPC and reported relative to poly(1,4-butadiene) standards. For **1**, poly(octenamer) of $M_n = 57,000$ and $M_w/M_n = 1.3$ was obtained. For **6**, poly(norbornylene) of $M_n = 75,000$ and $M_w/M_n = 1.8$ was obtained. Polymer yields were greater than 90%. No vinyl addition products were evident by ^{13}C NMR attached proton test (APT).

Oligomerization of 1,9-decadiene by **1** and **6** with AlCl₃

In a typical reaction, compounds **1** or **6** and 5 equivalents of AlCl₃ were dissolved in 500 equivalents of neat 1,9-decadiene. The solution was stirred at ambient temperature under static vacuum for 12 hours with no obvious change. The excess monomer was removed under reduced pressure leaving a brown gum. ¹H NMR in CDCl₃ showed the gum to be only dimer by integration of internal versus terminal olefinic protons. ¹³C NMR of the product showed both *cis* and *trans* internal olefins. No vinyl addition products were evident by ¹³C NMR attached proton test (APT). The yields of these reactions were less than 10 % dimer relative to monomer.

Thermolysis Kinetics

The general procedures for studying the kinetics of the thermolysis of (TMS₂pda)W(NPh)(CX₂C(CH₃)₃)₂ (X=H, **13**; X=D, **13-d₄**) follow. In a dry box, compound **13** (approx. 25 mg) was massed and placed in an NMR tube fitted with a screw-teflon cap (Aldrich). The solvent toluene-*d*₈ was added by syringe to give a 0.5-0.6 mL solution colored dark yellow-brown. Concentrations were typically 0.06 ± 0.005 M. Trimethylphosphine (76.08 g/mol, 0.735 g/ml) was added by microsyringe to the solution when necessary.

The kinetics were examined by ¹H NMR spectra of the sample. A specified temperature was established and allowed to equilibrate for five minutes. The sample was then inserted into the probe, and the deuterium lock signal was set and the sample shimmed. An initial spectrum was obtained to check the samples contents and to set the gain level. For the Varian Gemini-300 NMR spectrometer, the following parameters were set in experiment 4 (the largest writeable data block) to take a spectrum at a specified time interval: GAIN = Y and PAD(1)=0,Δt,Δt,Δt,Δt,Δt... where Δt is equal to the time interval minus 60 in seconds (i.e. for 10 minute interval, Δt = 600-60 sec = 540 sec). The 60 seconds allow for the one-minute data acquisition time. Setting GAIN = Y disables the

autogain program. The arrayed pulse sequence is then started to give up to 18 spectra. After reaction, the metallacycle solutions were dark yellow-brown and the alkylidene solutions were dark orange.

The rate was observed by the decrease in peak intensity of the neopentyl *t*-butyl (s, 18 protons) and the trimethylsilyl (s, 18 protons) resonances of **13**. To set the arrayed spectra to an absolute vertical intensity, the command 'ai' was entered. The rate was obtained by plotting the natural logarithm of peak intensity for the neopentyl and TMS groups versus time to obtain k_{NP} and k_{TMS} , sec^{-1} from the slope ($-k$). The values for k_{NP} and k_{TMS} agreed within 3% and were averaged to obtain k_{ave} . Optimally, three rate constants were obtained over a temperature range of 80 °C to 110 °C and were averaged to obtain k_{ave} at each temperature of 80, 90, 100 and 110 °C. A standard Eyring plot ($\ln(k/T)$ versus $1/T$) was made to obtain the activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ by the slope = $-\Delta H^\ddagger/R$ and the y-intercept = $23.76 + \Delta S^\ddagger/R$, where $R = 1.987 \text{ cal/molK}$. Confidence intervals of 95% for k are reported as $1.96(\text{standard deviation})(N)^{-1/2}$, where N is the number of determinations.¹²⁵ Errors for $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are reported from the standard errors in the slope and the y-intercept multiplied by R given in the regression analysis by Microsoft Excel 5.0 spreadsheet program.¹²⁶

UV-VIS Spectroscopy Studies

UV-VIS spectra were obtained using a Perkin-Elmer 330 spectrophotometer. Quartz cells (10 mm cell path) with tight-fitting teflon plugs were used. Solutions of **12**, **13** and **17** were prepared in toluene and diluted to give concentrations of 1.66×10^{-4} , 6.25×10^{-4} and $8.3 \times 10^{-5} \text{ M}$, respectively and absorbances at λ_{max} were 0.787, 0.84(0.13) and 0.561, respectively. To obtain the PMe_3 adducts, 50 μL of phosphine was added to 3 mL of the solutions, and absorbances for **18**, **19**, and **13** with PMe_3 were 0.500, 0.36 and 0.66(0.07). Values for λ_{max} and molar absorptivity are given in Table 3.2.

Mass Spectrometry of Neopentane- d_4

After samples of **13- d_4** were thermolyzed under specified conditions, the volatiles were vacuum transferred to teflon-sealed storage tubes cooled with liquid nitrogen. The volatiles consisted of argon, neopentane, toluene or benzene and PMe_3 if present. Samples were submitted for GC-CIMS. The volatiles were separated by gas chromatography using a GSQ 30m x 0.32 mm I.D. column by J&W Scientific, Folsom, CA. The carrier gas was He, and the oven temperature was a constant 150 °C. The mass spectra were determined on a Finnigan MAT95Q mass spectrometer, Finnigan MAT, San Jose, CA. The analytes were ionized by methane chemical ionization, and mass resolution was 1000. Mass spectral results are summarized in Table 3.3.

Deuterium NMR Spectroscopy

The ^2H NMR studies were performed on a Varian VXR-300. The instrument was tuned to deuterium (46.044 MHz) by (1) establishing a lock and shimming on a deuterated solvent sample, (2) reestablishing the lock signal by adjusting Z0 with the lock turned off, (3) tuning the probe with the yellow 30-60 MHz wave matching loop, the lock disengaged by pushing up the yellow stick and the "B" stick inserted to attenuate the frequency signal. Deuterium parameters were established with the "SU" command, and the observe coil was moved to the tuning socket. The frequency was tuned by adjusting the green and blue tuning sticks until a minimum tuning signal was obtained. Samples were run in non-deuterated toluene and referenced to a C_6D_6 internal standard (δ 7.30), and more than 5000 pulses were taken on each sample to increase the S/N ratio.

APPENDIX A
TABLES OF CRYSTALLOGRAPHIC DATA

Crystallographic Data for TpMo(CHCPh(CH₃)₂)(NAr)(OTf), **1**

Table A.1: Crystallographic data.

A. Crystal data (298 K)

<i>a</i> , Å	1 10.434(2)
<i>b</i> , Å	13.699(2)
<i>c</i> , Å	25.148(4)
<i>V</i> , Å ³	3595(1)
<i>d</i> _{calc} , g cm ⁻³ (298 K)	1.415
Empirical formula	C ₃₂ H ₃₉ BN ₇ O ₃ F ₃ SMo
Formula wt, g	765.51
Crystal system	Orthorhombic
Space group	P 2 ₁ 2 ₁ 2 ₁
<i>Z</i>	4
F(000), electrons	1576
Crystal size (mm ³)	0.68 x 0.10 x 0.10

B. Data collection (298 K)

Radiation, λ (Å)	Mo-K α , 0.71073															
Mode	ω -scan															
Scan range	Symmetrically over 1.2° about K $\alpha_{1,2}$ maximum															
Background	offset 1.0 and -1.0 in ω from K $\alpha_{1,2}$ maximum															
Scan rate, deg. min. ⁻¹	3 – 6															
2 θ range, deg.	3 – 50															
Range of $h\ k\ l$	<table><tr><td>0</td><td>≤</td><td>h</td><td>≤</td><td>12</td></tr><tr><td>0</td><td>≤</td><td>k</td><td>≤</td><td>16</td></tr><tr><td>0</td><td><</td><td>l</td><td><</td><td>29</td></tr></table>	0	≤	h	≤	12	0	≤	k	≤	16	0	<	l	<	29
0	≤	h	≤	12												
0	≤	k	≤	16												
0	<	l	<	29												

Total reflections measured	3603
Unique reflections	3575
Absorption coeff. μ (Mo-K _α), mm ⁻¹	0.48
Min. & Max. Transmission	0.951, 0.960

C. Structure refinement

<i>S</i> , Goodness-of-fit	1.48
Reflections used, <i>I</i> > 2σ(<i>I</i>)	2489
No. of variables	437
<i>R</i> , w <i>R</i> * (%)	5.30, 5.46
<i>R</i> _{int} . (%)	4.95
Max. shift/esd	0.0006

Table A.1 continued.

min. peak in diff. four. map ($\text{e } \text{\AA}^{-3}$)	-0.54
max. peak in diff. four. map ($\text{e } \text{\AA}^{-3}$)	0.50

* Relevant expressions are as follows, where in the footnote F_o and F_c represent, respectively, the observed and calculated structure-factor amplitudes.

Function minimized was $w(|F_o| - |F_c|)^2$, where $w = (\sigma(F))^{-2}$

$$R = \sum(|F_o| - |F_c|) / \sum |F_o|$$

$$wR = [\sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}$$

$$S = [\sum w(|F_o| - |F_c|)^2 / (m-n)]^{1/2}$$

Table A.2: Fractional coordinates and equivalent isotropic^a thermal parameters ($\text{\AA}^2$) for the non-H atoms of compound **1**.

Atom	x	y	z	U
Mo	0.02932(9)	0.06468(6)	0.11559(3)	0.0288(2)
S	0.2775(3)	0.1472(3)	0.1893(2)	0.0614(13)
F1	0.354(2)	0.2176(12)	0.2772(6)	0.236(10)
F2	0.245(2)	0.0858(10)	0.2851(4)	0.201(8)
F3	0.158(2)	0.2210(11)	0.2684(5)	0.187(9)
O1	0.1602(7)	0.0942(6)	0.1781(3)	0.043(3)
O2	0.2804(9)	0.2433(7)	0.1674(4)	0.075(4)
O3	0.3881(9)	0.0893(9)	0.1845(6)	0.131(6)
N	0.0679(7)	-0.0592(6)	0.1083(3)	0.036(3)
N1	-0.0468(8)	0.2193(6)	0.1344(3)	0.039(3)
N2	-0.1711(9)	0.2343(7)	0.1456(3)	0.040(3)
N3	-0.1466(8)	0.0698(8)	0.0699(3)	0.039(3)
N4	-0.2606(8)	0.0980(6)	0.0918(4)	0.039(3)
N5	-0.1054(9)	0.0331(6)	0.1865(4)	0.041(3)
N6	-0.2238(9)	0.0731(8)	0.1893(3)	0.045(3)
B	-0.2661(14)	0.1492(10)	0.1481(5)	0.050(5)
C1	0.1267(10)	0.1205(8)	0.0569(4)	0.028(3)
C2	0.2187(10)	0.0892(7)	0.0143(4)	0.036(4)
C3	0.3115(12)	0.1752(8)	0.0034(5)	0.052(4)
C4	0.2995(11)	0.0032(8)	0.0321(5)	0.049(4)
C5	0.1382(9)	0.0680(9)	-0.0352(3)	0.035(3)
C6	0.0661(11)	0.1406(10)	-0.0588(5)	0.054(5)
C7	-0.0121(12)	0.1213(11)	-0.1014(5)	0.070(6)
C8	-0.0198(15)	0.0282(12)	-0.1218(5)	0.084(6)
C9	0.0498(15)	-0.0435(12)	-0.0986(6)	0.089(7)
C10	0.1277(12)	-0.0246(9)	-0.0564(5)	0.062(5)
C11	0.0880(10)	-0.1598(7)	0.1101(5)	0.035(3)
C12	-0.0007(13)	-0.2232(8)	0.0866(5)	0.058(5)
C13	0.018(2)	-0.3224(8)	0.0922(5)	0.077(6)
C14	0.121(2)	-0.3596(9)	0.1181(6)	0.082(6)
C15	0.210(2)	-0.2976(10)	0.1389(5)	0.076(6)
C16	0.1967(12)	-0.1968(8)	0.1364(4)	0.049(4)
C17	0.3005(13)	-0.1323(10)	0.1613(5)	0.059(5)
C18	0.297(2)	-0.1426(12)	0.2217(5)	0.092(7)
C19	0.4320(11)	-0.1515(10)	0.1398(6)	0.074(6)
C20	-0.1187(13)	-0.1839(9)	0.0594(5)	0.057(5)
C21	-0.137(2)	-0.2303(11)	0.0048(6)	0.098(7)
C22	-0.237(2)	-0.1908(14)	0.0920(6)	0.115(9)
C23	0.0115(12)	0.3092(8)	0.1337(4)	0.047(4)
C24	-0.0788(13)	0.3777(9)	0.1461(5)	0.059(5)
C25	-0.1918(13)	0.3295(9)	0.1525(4)	0.051(5)
C26	-0.1773(12)	0.0456(8)	0.0202(5)	0.045(4)
C27	-0.3051(13)	0.0495(11)	0.0103(6)	0.062(5)
C28	-0.3564(11)	0.0861(9)	0.0579(6)	0.058(5)
C29	-0.0977(14)	-0.0306(9)	0.2248(4)	0.058(5)

Table A.2 continued.

C30	-0.2101(13)	-0.0339(11)	0.2537(5)	0.069(6)
C31	-0.2881(14)	0.0372(10)	0.2306(6)	0.070(6)
C32	0.260(3)	0.1658(13)	0.2602(8)	0.134(13)

For anisotropic atoms, the U value is U_{eq} , calculated as $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* A_{ij}$ where A_{ij} is the dot product of the i^{th} and j^{th} direct space unit cell vectors.

Table A.3: Bond Lengths (Å) and Angles (°) for the non-H atoms of compound 1.

1	2	3	1-2	1-2-3
O1	Mo	N	2.121(7)	96.5(3)
O1	Mo	N1		84.0(3)
O1	Mo	N3		158.8(3)
O1	Mo	N5		81.7(3)
N	Mo	N1	1.753(8)	170.8(3)
N	Mo	N3		99.8(4)
N	Mo	N5		92.2(3)
N	Mo	C1		100.5(4)
N1	Mo	N3	2.311(8)	77.7(3)
N1	Mo	N5		78.8(3)
N1	Mo	C1		88.5(4)
N3	Mo	N5	2.167(8)	84.3(3)
N3	Mo	C1		91.5(4)
N5	Mo	C1	2.311(9)	167.2(4)
C1	Mo	O1	1.949(10)	98.7(4)
O1	S	O2	1.451(8)	113.9(5)
O2	S	O3	1.427(10)	118.0(7)
O3	S	O1	1.406(11)	113.1(6)
C32	F1		1.28(3)	
C32	F2		1.27(2)	
C32	F3		1.32(3)	
Mo	O1	S		141.5(5)
C11	N	Mo	1.396(12)	170.9(7)
N2	N1	C23	1.344(12)	107.0(8)
N2	N1	Mo		121.0(6)
C23	N1	Mo	1.373(14)	131.9(7)
B	N2	C25	1.53(2)	129.4(10)
B	N2	N1		121.1(9)
C25	N2	N1	1.333(15)	109.4(9)
N4	N3	C26	1.366(12)	103.8(8)
N4	N3	Mo		122.2(6)
C26	N3	Mo	1.332(14)	133.9(7)
B	N4	C28	1.58(2)	127.1(10)
B	N4	N3		121.2(9)
C28	N4	N3	1.32(2)	111.3(9)
N6	N5	C29	1.354(13)	106.8(10)
N6	N5	Mo		121.3(7)
C29	N5	Mo	1.303(14)	131.2(8)
B	N6	C31	1.53(2)	129.3(11)
B	N6	N5		120.2(9)
C31	N6	N5	1.33(2)	110.5(10)
N2	B	N4		106.1(9)
N2	B	N6		111.0(10)
N4	B	N6		107.0(10)
C2	C1	Mo	1.501(14)	139.6(8)

Table A.3 continued.

C3	C2	C4	1.55(2)	107.2(9)
C3	C2	C5		110.1(9)
C3	C2	C1		107.9(8)
C4	C2	C5	1.516(15)	113.5(9)
C4	C2	C1		111.5(9)
C5	C2	C1	1.529(14)	106.5(8)
C6	C5	C10	1.38(2)	117.0(10)
C6	C5	C2		120.7(10)
C10	C5	C2	1.38(2)	122.1(10)
C7	C6	C5	1.37(2)	121.3(12)
C8	C7	C6	1.38(2)	120.3(13)
C9	C8	C7	1.35(2)	118.6(13)
C10	C9	C8	1.36(2)	121.2(14)
C5	C10	C9		121.5(12)
C12	C11	C16	1.40(2)	120.5(9)
C12	C11	N		120.1(9)
C16	C11	N	1.41(2)	119.4(9)
C13	C12	C20	1.38(2)	121.0(12)
C13	C12	C11		118.2(12)
C20	C12	C11	1.51(2)	120.6(9)
C14	C13	C12	1.36(2)	122.1(13)
C15	C14	C13	1.36(2)	119.2(12)
C16	C15	C14	1.39(2)	122.6(13)
C17	C16	C11	1.53(2)	123.7(10)
C17	C16	C15		119.1(11)
C11	C16	C15		117.2(11)
C18	C17	C19	1.53(2)	111.3(11)
C18	C17	C16		109.8(11)
C19	C17	C16	1.50(2)	113.5(11)
C21	C20	C22	1.52(2)	111.5(13)
C21	C20	C12		111.3(11)
C22	C20	C12	1.49(2)	113.9(12)
C24	C23	N1	1.37(2)	107.9(10)
C25	C24	C23	1.36(2)	107.0(11)
N2	C25	C24		108.6(11)
C27	C26	N3	1.36(2)	113.5(11)
C28	C27	C26	1.40(2)	103.5(11)
N4	C28	C27		107.7(10)
C30	C29	N5	1.38(2)	111.1(12)
C31	C30	C29	1.40(2)	104.7(12)
N6	C31	C30		106.8(12)
F1	C32	F2		114.(2)
F1	C32	F3		104.(2)
F2	C32	F3		108.(2)

Table A.4: Anisotropic thermal parameters^a for the non-H atoms of compound 1.

Atom	U11	U22	U33	U12	U13	U23
Mo	0.0263(4)	0.0297(4)	0.0305(4)	-0.0012(5)	-0.0015(5)	-0.0032(5)
S	0.042(2)	0.065(2)	0.078(3)	-0.009(2)	-0.014(2)	-0.002(2)
F1	0.32(2)	0.21(2)	0.182(13)	-0.11(2)	-0.155(15)	-0.019(12)
F2	0.37(2)	0.150(11)	0.079(7)	-0.036(15)	-0.085(10)	0.025(8)
F3	0.33(2)	0.120(11)	0.109(9)	-0.025(13)	0.073(13)	-0.048(9)
O1	0.035(4)	0.056(6)	0.039(4)	-0.007(4)	-0.007(4)	-0.002(4)
O2	0.060(6)	0.080(7)	0.084(7)	-0.036(5)	-0.012(6)	0.023(6)
O3	0.039(6)	0.111(10)	0.244(15)	-0.004(7)	-0.011(8)	-0.034(10)
N	0.034(4)	0.043(5)	0.031(4)	0.001(4)	-0.005(4)	0.003(5)
N1	0.029(5)	0.043(5)	0.044(5)	0.006(5)	-0.003(4)	-0.003(4)
N2	0.037(6)	0.039(5)	0.044(5)	0.007(5)	0.008(5)	-0.001(5)
N3	0.027(5)	0.039(5)	0.052(6)	-0.005(5)	-0.009(4)	-0.009(6)
N4	0.023(5)	0.038(5)	0.055(6)	-0.005(4)	-0.013(5)	0.017(4)
N5	0.041(6)	0.042(6)	0.041(5)	0.004(4)	0.006(5)	-0.000(4)
N6	0.041(6)	0.045(6)	0.050(6)	0.001(6)	-0.004(5)	0.016(6)
B	0.040(8)	0.056(9)	0.053(9)	0.033(8)	0.010(7)	0.005(8)
C1	0.026(6)	0.027(6)	0.030(6)	0.008(5)	0.003(5)	-0.010(5)
C2	0.036(6)	0.028(7)	0.043(6)	-0.002(5)	-0.000(5)	-0.004(5)
C3	0.053(8)	0.056(8)	0.048(7)	-0.010(7)	0.012(7)	-0.007(6)
C4	0.053(8)	0.038(7)	0.054(8)	0.014(6)	0.005(7)	0.012(6)
C5	0.032(5)	0.037(6)	0.035(5)	0.007(6)	0.002(5)	-0.004(6)
C6	0.055(9)	0.067(8)	0.040(7)	-0.003(7)	0.003(6)	0.005(6)
C7	0.048(9)	0.101(11)	0.060(9)	0.003(8)	-0.013(7)	0.026(8)
C8	0.083(10)	0.129(13)	0.039(8)	-0.021(11)	-0.032(8)	-0.017(8)
C9	0.089(12)	0.095(12)	0.082(10)	0.009(10)	-0.026(10)	-0.017(9)
C10	0.057(9)	0.061(9)	0.067(9)	0.019(7)	-0.020(8)	-0.017(7)
C11	0.037(6)	0.024(5)	0.045(7)	-0.004(5)	0.017(6)	0.006(6)
C12	0.080(12)	0.028(6)	0.066(8)	0.003(7)	0.005(8)	-0.005(6)
C13	0.106(12)	0.028(6)	0.097(10)	-0.016(8)	-0.010(10)	-0.003(6)
C14	0.116(13)	0.040(7)	0.091(11)	0.021(8)	-0.009(12)	0.007(9)
C15	0.092(11)	0.053(9)	0.084(10)	0.001(9)	-0.006(9)	0.005(8)
C16	0.061(8)	0.038(7)	0.047(7)	0.013(6)	0.016(7)	0.010(6)
C17	0.053(9)	0.074(9)	0.050(8)	0.013(8)	-0.006(7)	0.002(7)
C18	0.112(14)	0.119(13)	0.046(8)	0.026(12)	-0.006(9)	-0.002(9)
C19	0.051(9)	0.091(11)	0.081(10)	0.013(8)	-0.011(7)	-0.005(8)
C20	0.068(9)	0.030(6)	0.072(10)	-0.015(7)	-0.004(8)	-0.012(7)
C21	0.12(2)	0.081(12)	0.093(11)	-0.033(11)	-0.035(11)	-0.003(10)
C22	0.100(14)	0.15(2)	0.092(13)	0.016(15)	-0.032(12)	-0.018(12)
C23	0.061(9)	0.042(6)	0.039(6)	-0.020(7)	0.001(6)	-0.016(5)
C24	0.077(10)	0.047(7)	0.052(8)	0.008(8)	0.006(7)	-0.021(6)
C25	0.067(9)	0.052(8)	0.035(7)	0.004(7)	-0.013(7)	-0.002(6)
C26	0.050(8)	0.035(8)	0.048(7)	-0.010(6)	-0.012(6)	-0.004(6)
C27	0.051(9)	0.061(10)	0.074(9)	-0.013(8)	-0.047(8)	0.004(8)

Table A.4 continued.

C28	0.032(7)	0.048(9)	0.095(10)	-0.013(6)	-0.013(8)	0.007(8)
C29	0.081(10)	0.065(9)	0.028(6)	-0.003(7)	0.003(7)	0.012(6)
C30	0.069(10)	0.088(12)	0.050(8)	-0.006(9)	0.030(7)	0.022(7)
C31	0.071(11)	0.070(11)	0.067(9)	-0.015(8)	0.032(9)	0.004(8)
C32	0.25(3)	0.053(14)	0.10(2)	-0.04(2)	-0.09(2)	-0.009(11)

^a U_{ij} are the mean-square amplitudes of vibration in Å²

from the general temperature factor expression

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + \\ + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$$

Table A.5: Fractional coordinates and isotropic thermal parameters ($\text{\AA}^2$) for the H atoms of compound **1**.

Atom	x	y	z	U
H	-0.37214	0.18044	0.15262	0.08
H1	0.096(8)	0.185(7)	0.055(3)	0.03(3)
H3a	0.37168	0.15671	-0.02369	0.08
H3b	0.3569	0.19105	0.03545	0.08
H3c	0.26364	0.23104	-0.0083	0.08
H4a	0.24428	-0.05139	0.03909	0.08
H4b	0.34562	0.01982	0.06384	0.08
H4c	0.3591	-0.01378	0.00451	0.08
H6a	0.07151	0.20603	-0.04529	0.08
H7a	-0.06228	0.17285	-0.11673	0.08
H8a	-0.07188	0.01535	-0.1525	0.08
H9a	0.04231	-0.10921	-0.1115	0.08
H10a	0.17702	-0.07652	-0.04087	0.08
H13a	-0.04483	-0.36626	0.078	0.08
H14a	0.13266	-0.42892	0.12141	0.08
H15a	0.28386	-0.32533	0.15564	0.08
H17a	0.28129	-0.06584	0.15221	0.08
H18a	0.36302	-0.1023	0.23699	0.08
H18b	0.31193	-0.20942	0.2314	0.08
H18c	0.21514	-0.12212	0.23486	0.08
H19a	0.43003	-0.14466	0.10186	0.08
H19b	0.45822	-0.21657	0.14891	0.08
H19c	0.49162	-0.10548	0.15455	0.08
H20a	-0.10343	-0.11536	0.05468	0.08
H21a	-0.05927	-0.22468	-0.01538	0.08
H21b	-0.20519	-0.19765	-0.01366	0.08
H21c	-0.15834	-0.29805	0.00909	0.08
H22a	-0.22254	-0.16092	0.12598	0.08
H22b	-0.25924	-0.25824	0.09695	0.08
H22c	-0.3061	-0.15785	0.07421	0.08
H23a	0.09962	0.32182	0.125150	0.08
H24a	-0.06499	0.4465	0.15038	0.08
H25a	-0.27267	0.3594	0.16055	0.08
H26a	-0.1155	0.02687	-0.00621	0.08
H27a	-0.35048	0.03089	-0.02132	0.08
H28a	-0.44484	0.10094	0.06469	0.08
H29a	-0.02387	-0.0704	0.23175	0.08
H30a	-0.23087	-0.07599	0.28301	0.08
H31a	-0.37108	0.05777	0.24268	0.08

Table A.6: Bond Lengths (Å) and Angles (°) of the H atoms of compound 1.

<u>1</u>	<u>2</u>	<u>3</u>	<u>1-2</u>	<u>1-2-3</u>
H	B	N2	1.192(14)	109.4(10)
H	B	N4		106.2(10)
H	B	N6		116.5(11)
H1	C1	C2	0.94(9)	116.(5)
H1	C1	Mo		104.(5)
H3a	C3	H3b	0.960(12)	109.5(12)
H3a	C3	H3c		109.5(11)
H3a	C3	C2		109.5(10)
H3b	C3	H3c	0.960(12)	109.5(11)
H3b	C3	C2		109.4(10)
H3c	C3	C2	0.960(12)	109.5(11)
H4a	C4	H4b	0.960(11)	109.5(11)
H4a	C4	H4c		109.5(10)
H4a	C4	C2		109.0(10)
H4b	C4	H4c	0.960(12)	109.5(11)
H4b	C4	C2		109.9(9)
H4c	C4	C2	0.960(12)	109.5(10)
H6a	C6	C7	0.960(13)	119.3(12)
H6a	C6	C5		119.3(11)
H7a	C7	C8	0.960(14)	119.9(13)
H7a	C7	C6		119.8(14)
H8a	C8	C9	0.960(14)	121.(2)
H8a	C8	C7		120.(2)
H9a	C9	C10	0.96(2)	119.4(15)
H9a	C9	C8		119.3(15)
H10a	C10	C5	0.960(13)	118.8(12)
H10a	C10	C9		119.7(13)
H13a	C13	C14	0.960(14)	119.2(11)
H13a	C13	C12		118.7(14)
H14a	C14	C15	0.960(13)	120.(2)
H14a	C14	C13		120.6(14)
H15a	C15	C16	0.960(15)	119.4(14)
H15a	C15	C14		117.9(13)
H17a	C17	C18	0.960(13)	108.6(12)
H17a	C17	C19		105.8(11)
H17a	C17	C16		107.6(11)
H18a	C18	H18b	0.96(2)	109.5(15)
H18a	C18	H18c		109.5(14)
H18a	C18	C17		109.2(13)
H18b	C18	H18c	0.96(2)	109.5(15)
H18b	C18	C17		109.6(12)
H18c	C18	C17	0.96(2)	109.6(13)
H19a	C19	H19b	0.960(14)	109.5(13)
H19a	C19	H19c		109.5(13)
H19a	C19	C17		108.8(11)
H19b	C19	H19c	0.960(13)	109.5(12)

Table A.6 continued.

H19b	C19	C17		109.8(12)
H19c	C19	C17	0.960(13)	109.9(12)
H20a	C20	C21	0.960(12)	108.6(12)
H20a	C20	C22		105.5(13)
H20a	C20	C12		105.7(12)
H21a	C21	H21b	0.96(2)	109.5(15)
H21a	C21	H21c		109.(2)
H21a	C21	C20		109.6(15)
H21b	C21	H21c	0.96(2)	109.(2)
H21b	C21	C20		109.5(14)
H21c	C21	C20	0.96(2)	109.3(13)
H22a	C22	H22b	0.96(2)	109.(2)
H22a	C22	H22c		109.(2)
H22a	C22	C20		109.4(14)
H22b	C22	H22c	0.96(2)	109.(2)
H22b	C22	C20		109.4(15)
H22c	C22	C20	0.96(2)	109.6(14)
H23a	C23	C24	0.960(12)	126.0(11)
H23a	C23	N1		126.1(11)
H24a	C24	C25	0.960(12)	126.4(13)
H24a	C24	C23		126.7(13)
H25a	C25	N2	0.960(13)	125.9(12)
H25a	C25	C24		125.5(12)
H26a	C26	C27	0.960(12)	122.9(12)
H26a	C26	N3		123.6(11)
H27a	C27	C28	0.960(14)	127.8(13)
H27a	C27	C26		128.8(14)
H28a	C28	N4	0.960(12)	125.8(13)
H28a	C28	C27		126.5(13)
H29a	C29	C30	0.960(13)	124.6(12)
H29a	C29	N5		124.3(12)
H30a	C30	C31	0.960(13)	127.4(14)
H30a	C30	C29		128.0(14)
H31a	C31	N6	0.960(15)	126.3(14)
		H31a	C31 C30	126.9(14)

Crystallographic Data for $\text{TpMo}(\text{O})(\text{NAr})(\text{CH}_2\text{CPh}(\text{CH}_3)_2)$, 2Table A.7: Crystallographic data.

A. Crystal data (298 K)	2
a , Å	9.417(1)
b , Å	12.816(1)
c , Å	14.698(2)
α , deg.	100.73(1)
β , deg.	94.71(1)
γ , deg.	108.89(1)
V , Å ³	1629.5(3)
d_{calc} , g cm ⁻³ (298 K)	1.291
Empirical formula	C ₃₁ H ₄₀ BN ₇ OMo
Formula wt, g	633.45
Crystal system	Triclinic
Space group	P 1bar
Z	2
$F(000)$, electrons	660
Crystal size (mm ³)	0.46 x 0.28 x 0.27
B. Data collection (298 K)	
Radiation, λ (Å)	Mo-K α , 0.71073
Mode	ω -scan
Scan range	Symmetrically over 1.2° about K $\alpha_{1,2}$ maximum
Background	offset 1.0 and -1.0 in ω from K $\alpha_{1,2}$ maximum
Scan rate, deg. min. ⁻¹	4 – 8
2 θ range, deg.	3 – 55
Range of $h\ k\ l$	$\begin{array}{rclcl} 0 & \leq & h & \leq & 12 \\ -16 & \leq & k & \leq & 16 \\ -19 & \leq & l & \leq & 19 \end{array}$
Total reflections measured	7953
Unique reflections	7495
Absorption coeff. μ (Mo-K α), cm ⁻¹	6765
Min. & Max. Transmission	0.882, 0.904
C. Structure refinement	
S , Goodness-of-fit	1.44
Reflections used, $I > 2\sigma(I)$	6765
No. of variables	530
R , wR^* (%)	3.23, 4.11
R_{int} (%)	1.08
Max. shift/esd	0.001

Table A.7 continued.

min. peak in diff. four. map ($\text{e } \text{\AA}^{-3}$)	-0.35
max. peak in diff. four. map ($\text{e } \text{\AA}^{-3}$)	0.35

* Relevant expressions are as follows, where in the footnote F_o and F_c represent, respectively, the observed and calculated structure-factor amplitudes.

Function minimized was $w(|F_o| - |F_c|)^2$, where $w = (\sigma(F))^{-2}$

$$R = \sum(|F_o| - |F_c|) / \sum |F_o|$$

$$wR = [\sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}$$

$$S = [\sum w(|F_o| - |F_c|)^2 / (m-n)]^{1/2}$$

Table A.8: Fractional coordinates and equivalent isotropic^a thermal parameters ($\text{\AA}^2$) for the non-H atoms of compound 2.

Atom	x	y	z	U
Mo	0.20884(2)	0.298290(10)	0.174370(10)	0.03119(7)
O	0.0254(2)	0.2613(2)	0.19504(12)	0.0504(7)
N	0.3054(2)	0.27178(14)	0.27027(12)	0.0351(6)
N1	0.4195(2)	0.3583(2)	0.09393(12)	0.0390(6)
N1'	0.4165(2)	0.3103(2)	0.00279(13)	0.0418(7)
N2	0.1068(2)	0.31379(14)	0.03037(12)	0.0375(6)
N2'	0.1443(2)	0.2737(2)	-0.05291(12)	0.0434(7)
N3	0.2095(2)	0.13961(14)	0.08514(13)	0.0401(6)
N3'	0.2263(2)	0.1219(2)	-0.00661(14)	0.0447(7)
B	0.2707(3)	0.2217(2)	-0.0546(2)	0.0468(10)
C1	0.5591(3)	0.4348(2)	0.1224(2)	0.0473(9)
C2	0.6456(3)	0.4363(2)	0.0510(2)	0.0565(11)
C3	0.5519(3)	0.3566(2)	-0.0235(2)	0.0548(11)
C4	-0.0080(3)	0.3492(2)	0.0107(2)	0.0452(8)
C5	-0.0456(3)	0.3321(2)	-0.0860(2)	0.0570(10)
C6	0.0531(3)	0.2840(2)	-0.1229(2)	0.0543(10)
C7	0.1845(3)	0.0397(2)	0.1097(2)	0.0544(10)
C8	0.1861(4)	-0.0409(2)	0.0339(3)	0.0706(13)
C9	0.2120(3)	0.0132(2)	-0.0376(2)	0.0634(12)
C10	0.2650(3)	0.4820(2)	0.2165(2)	0.0405(8)
C11	0.3082(3)	0.5531(2)	0.3189(2)	0.0449(8)
C12	0.4612(5)	0.5544(3)	0.3642(3)	0.078(2)
C13	0.1901(6)	0.5041(3)	0.3774(3)	0.082(2)
C14	0.3207(3)	0.6740(2)	0.31301(14)	0.0422(8)
C15	0.4389(4)	0.7409(2)	0.2766(2)	0.0581(11)
C16	0.4480(5)	0.8485(3)	0.2670(2)	0.0731(14)
C17	0.3386(5)	0.8914(3)	0.2935(2)	0.075(2)
C18	0.2220(4)	0.8279(3)	0.3302(2)	0.0708(14)
C19	0.2115(3)	0.7203(3)	0.3395(2)	0.0574(11)
C20	0.3595(2)	0.2283(2)	0.33968(14)	0.0365(7)
C21	0.5094(3)	0.2262(2)	0.3455(2)	0.0437(8)
C22	0.5586(3)	0.1817(2)	0.4158(2)	0.0544(10)
C23	0.4647(4)	0.1386(2)	0.4770(2)	0.0577(11)
C24	0.3204(3)	0.1395(2)	0.4706(2)	0.0540(10)
C25	0.2623(3)	0.1842(2)	0.4026(2)	0.0444(9)
C26	0.6094(3)	0.2685(3)	0.2761(2)	0.0569(11)
C27	0.7628(5)	0.3568(4)	0.3227(4)	0.093(2)
C28	0.6306(6)	0.1712(5)	0.2079(4)	0.100(2)
C29	0.1017(3)	0.1844(3)	0.3968(2)	0.0606(12)
C30	-0.0115(5)	0.0652(5)	0.3606(5)	0.104(3)
C31	0.0709(7)	0.2412(6)	0.4902(4)	0.106(3)

^aFor anisotropic atoms, the U value is U_{eq} , calculated as $U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* A_{ij}$ where A_{ij} is the dot product of the i^{th} and j^{th} direct space unit cell vectors.

Table A.9: Bond Lengths (Å) and Angles (°) for the non-H atoms of compound 2.

1	2	3	1-2	1-2-3
O	Mo	N	1.706(2)	103.68(9)
O	Mo	N1		158.69(8)
O	Mo	N2		84.04(8)
O	Mo	N3		101.76(8)
N	Mo	N1	1.760(2)	97.56(8)
N	Mo	N2		168.68(8)
N	Mo	N3		90.07(8)
N	Mo	C10		101.46(9)
N1	Mo	N2	2.379(2)	74.68(6)
N1	Mo	N3		76.13(6)
N1	Mo	C10		80.49(9)
N2	Mo	N3	2.321(2)	80.14(7)
N2	Mo	C10		85.59(8)
N3	Mo	C10	2.207(2)	155.10(8)
C10	Mo	O	2.191(2)	96.89(10)
C20	N	Mo	1.386(3)	168.07(13)
N1'	N1	C1	1.360(3)	105.6(2)
N1'	N1	Mo		122.32(11)
C1	N1	Mo	1.337(3)	132.0(2)
B	N1'	C3	1.526(3)	129.8(2)
B	N1'	N1		120.4(2)
C3	N1'	N1	1.342(3)	109.8(2)
N2'	N2	C4	1.357(3)	106.6(2)
N2'	N2	Mo		124.3(2)
C4	N2	Mo	1.332(4)	128.6(2)
B	N2'	C6	1.541(4)	130.9(2)
B	N2'	N2		119.6(2)
C6	N2'	N2	1.338(4)	109.5(2)
N3'	N3	C7	1.356(3)	106.6(2)
N3'	N3	Mo		126.7(2)
C7	N3	Mo	1.347(3)	126.6(2)
B	N3'	C9	1.531(4)	130.7(2)
B	N3'	N3		120.0(2)
C9	N3'	N3	1.341(4)	109.0(2)
N1'	B	N2'		108.5(2)
N1'	B	N3'		107.7(2)
N2'	B	N3'		108.6(2)
C2	C1	N1	1.379(4)	111.0(2)
C3	C2	C1	1.364(3)	104.9(2)
N1'	C3	C2		108.6(3)
C5	C4	N2	1.394(4)	110.3(2)
C6	C5	C4	1.367(5)	104.5(3)
N2'	C6	C5		109.1(2)
C8	C7	N3	1.376(4)	109.7(3)
C9	C8	C7	1.359(5)	105.5(3)
N3'	C9	C8		109.1(3)

Table A.9 continued.

C11	C10	Mo	1.552(3)	125.5(2)
C12	C11	C13	1.530(5)	107.9(3)
C12	C11	C14		109.2(2)
C12	C11	C10		111.2(3)
C13	C11	C14	1.509(5)	112.1(3)
C13	C11	C10		110.5(2)
C14	C11	C10	1.536(4)	106.1(2)
C15	C14	C19	1.382(4)	116.4(3)
C15	C14	C11		121.1(3)
C19	C14	C11	1.391(5)	122.4(2)
C16	C15	C14	1.387(5)	121.8(3)
C17	C16	C15	1.368(7)	120.4(3)
C18	C17	C16	1.357(5)	119.1(3)
C19	C18	C17	1.383(5)	121.0(4)
C14	C19	C18		121.4(3)
C21	C20	C25	1.417(4)	121.0(2)
C21	C20	N		119.7(2)
C25	C20	N	1.418(3)	119.2(2)
C22	C21	C26	1.386(4)	121.6(3)
C22	C21	C20		117.7(2)
C26	C21	C20	1.501(4)	120.7(2)
C23	C22	C21	1.376(4)	121.5(3)
C24	C23	C22	1.359(5)	120.7(3)
C25	C24	C23	1.397(4)	121.6(3)
C29	C25	C20	1.508(4)	121.8(2)
C29	C25	C24		120.7(2)
C20	C25	C24		117.5(3)
C27	C26	C28	1.526(4)	110.6(3)
C27	C26	C21		112.9(3)
C28	C26	C21	1.526(7)	111.4(3)
C30	C29	C31	1.517(5)	111.7(4)
C30	C29	C25		110.7(3)
C31	C29	C25	1.525(7)	111.9(3)

Table A.10: Anisotropic thermal parameters^a for the non-H atoms of compound 2.

Atom	U11	U22	U33	U12	U13	U23
Mo	0.03042(9)	0.03269(10)	0.03358(10)	0.01278(7)	0.00569(6)	0.01126(6)
O	0.0366(8)	0.0684(11)	0.0527(10)	0.0214(8)	0.0107(7)	0.0224(8)
N	0.0365(9)	0.0366(9)	0.0354(9)	0.0148(7)	0.0069(7)	0.0110(7)
N1	0.0399(9)	0.0364(9)	0.0401(9)	0.0110(7)	0.0088(7)	0.0098(7)
N1'	0.0464(10)	0.0438(10)	0.0404(9)	0.0187(8)	0.0152(8)	0.0125(8)
N2	0.0405(9)	0.0342(9)	0.0373(9)	0.0138(7)	0.0006(7)	0.0080(7)
N2'	0.0497(11)	0.0422(10)	0.0350(9)	0.0149(8)	-0.0010(8)	0.0057(8)
N3	0.0387(9)	0.0316(9)	0.0496(10)	0.0114(7)	0.0049(8)	0.0105(8)
N3'	0.0478(11)	0.0363(9)	0.0479(11)	0.0165(8)	0.0052(8)	0.0015(8)
B	0.054(2)	0.0474(14)	0.0387(13)	0.0194(12)	0.0089(11)	0.0044(11)
C1	0.0389(12)	0.0400(12)	0.0602(15)	0.0085(9)	0.0072(10)	0.0145(11)
C2	0.0406(13)	0.0544(15)	0.081(2)	0.0136(12)	0.0211(13)	0.0297(14)
C3	0.0531(14)	0.063(2)	0.059(2)	0.0235(13)	0.0268(12)	0.0250(13)
C4	0.0447(12)	0.0365(11)	0.0548(14)	0.0166(10)	-0.0024(10)	0.0110(10)
C5	0.0551(15)	0.0542(15)	0.059(2)	0.0177(12)	-0.0136(12)	0.0189(12)
C6	0.062(2)	0.0537(14)	0.0406(13)	0.0151(12)	-0.0069(11)	0.0091(11)
C7	0.0521(14)	0.0354(12)	0.076(2)	0.0129(10)	0.0075(13)	0.0195(12)
C8	0.072(2)	0.0297(12)	0.106(3)	0.0172(13)	0.006(2)	0.0084(14)
C9	0.067(2)	0.0421(14)	0.075(2)	0.0223(13)	0.0068(15)	-0.0068(13)
C10	0.0503(13)	0.0386(11)	0.0358(11)	0.0206(10)	0.0038(10)	0.0077(9)
C11	0.0599(14)	0.0368(11)	0.0359(11)	0.0163(10)	0.0027(10)	0.0059(9)
C12	0.100(3)	0.051(2)	0.072(2)	0.033(2)	-0.037(2)	-0.003(2)
C13	0.130(4)	0.055(2)	0.057(2)	0.020(2)	0.040(2)	0.013(2)
C14	0.0537(13)	0.0379(11)	0.0312(10)	0.0164(10)	-0.0008(9)	0.0010(8)
C15	0.071(2)	0.0485(14)	0.055(2)	0.0207(13)	0.0172(13)	0.0073(12)
C16	0.108(3)	0.048(2)	0.055(2)	0.015(2)	0.016(2)	0.0131(13)
C17	0.123(3)	0.048(2)	0.050(2)	0.037(2)	-0.011(2)	0.0012(13)
C18	0.084(2)	0.065(2)	0.065(2)	0.045(2)	-0.011(2)	-0.0061(15)
C19	0.057(2)	0.057(2)	0.0543(15)	0.0231(13)	0.0004(12)	0.0001(12)
C20	0.0415(11)	0.0365(10)	0.0344(10)	0.0172(9)	0.0024(8)	0.0096(8)
C21	0.0431(12)	0.0444(12)	0.0441(12)	0.0192(10)	-0.0005(9)	0.0073(9)
C22	0.0542(15)	0.057(2)	0.0535(14)	0.0275(12)	-0.0084(12)	0.0088(12)
C23	0.081(2)	0.0526(14)	0.0425(13)	0.0308(14)	-0.0102(13)	0.0122(11)
C24	0.074(2)	0.0542(14)	0.0396(12)	0.0252(13)	0.0080(12)	0.0208(11)
C25	0.0553(13)	0.0454(12)	0.0394(11)	0.0227(11)	0.0100(10)	0.0153(9)
C26	0.0410(13)	0.075(2)	0.065(2)	0.0284(13)	0.0105(11)	0.0247(14)
C27	0.061(2)	0.094(3)	0.106(3)	0.007(2)	0.014(2)	0.016(3)
C28	0.092(3)	0.111(3)	0.088(3)	0.026(3)	0.045(3)	0.005(3)
C29	0.061(2)	0.080(2)	0.066(2)	0.0355(15)	0.0295(13)	0.047(2)
C30	0.054(2)	0.112(4)	0.148(5)	0.017(2)	0.015(3)	0.058(4)
C31	0.125(4)	0.163(5)	0.091(3)	0.100(4)	0.064(3)	0.064(3)

^a U_{ij} are the mean-square amplitudes of vibration in Å² from the general temperature factor

expression $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$

Table A.11: Fractional coordinates and isotropic thermal parameters ($\text{\AA}^2$) for the H atoms of compound 2.

Atom	x	y	z	U
H	0.284(3)	0.191(2)	-0.133(2)	0.046(6)
H1	0.586(3)	0.478(2)	0.187(2)	0.052(7)
H2	0.736(4)	0.480(3)	0.056(2)	0.072(9)
H3	0.567(4)	0.329(3)	-0.087(2)	0.084(10)
H4	-0.051(3)	0.379(2)	0.061(2)	0.045(7)
H5	-0.116(3)	0.349(2)	-0.114(2)	0.054(7)
H6	0.065(3)	0.251(2)	-0.189(2)	0.058(8)
H7	0.165(4)	0.031(3)	0.167(2)	0.073(10)
H8	0.178(4)	-0.111(3)	0.032(2)	0.074(9)
H9	0.221(3)	-0.011(3)	-0.101(2)	0.067(9)
H10a	0.185(3)	0.487(2)	0.191(2)	0.047(7)
H10b	0.332(3)	0.514(2)	0.183(2)	0.060(8)
H12a	0.48515	0.59884	0.42728	0.08
H12b	0.45557	0.47838	0.3647	0.08
H12c	0.53883	0.58682	0.3289	0.08
H13a	0.21842	0.54901	0.44046	0.08
H13b	0.09335	0.50447	0.35147	0.08
H13c	0.18337	0.42782	0.37764	0.08
H15	0.517(3)	0.715(3)	0.262(2)	0.066(9)
H16	0.542(4)	0.893(3)	0.252(2)	0.085(11)
H17	0.344(4)	0.976(3)	0.293(2)	0.076(9)
H18	0.149(4)	0.856(3)	0.345(2)	0.093(12)
H19	0.133(4)	0.678(3)	0.364(2)	0.074(10)
H22	0.657(3)	0.172(2)	0.414(2)	0.067(8)
H23	0.502(4)	0.113(3)	0.522(2)	0.082(10)
H24	0.254(3)	0.109(2)	0.511(2)	0.064(8)
H26	0.568(4)	0.307(3)	0.248(2)	0.069(9)
H27a	0.74726	0.41721	0.36534	0.08
H27b	0.81975	0.32226	0.35653	0.08
H27c	0.81797	0.38638	0.27566	0.08
H28a	0.533	0.11662	0.17926	0.08
H28b	0.68514	0.20001	0.16029	0.08
H28c	0.68692	0.13589	0.24116	0.08
H29	0.087(3)	0.226(2)	0.356(2)	0.050(7)
H30a	0.01111	0.03207	0.30195	0.08
H30b	-0.00489	0.02029	0.40522	0.08
H30c	-0.11233	0.06781	0.35179	0.08
H31a	0.1444	0.31617	0.51099	0.08
H31b	-0.02919	0.24526	0.48246	0.08
H31c	0.07825	0.19775	0.53589	0.08

Table A.12: Bond Lengths (Å) and Angles (°) of the H atoms of compound 2.

<u>1</u>	<u>2</u>	<u>3</u>	<u>1-2</u>	<u>1-2-3</u>
H	B	N1'	1.18(3)	112.5(11)
H	B	N2'		108.8(14)
H	B	N3'		110.7(13)
H1	C1	C2	.98(2)	130.(2)
H1	C1	N1		119.(2)
H2	C2	C3	.85(3)	131.(2)
H2	C2	C1		124.(2)
H3	C3	N1'	.97(3)	119.(2)
H3	C3	C2		133.(2)
H4	C4	C5	.94(3)	131.(2)
H4	C4	N2		119.(2)
H5	C5	C6	.87(3)	129.(2)
H5	C5	C4		126.(2)
H6	C6	N2'	1.02(3)	117.(2)
H6	C6	C5		134.(2)
H7	C7	C8	.89(3)	128.(2)
H7	C7	N3		122.(2)
H8	C8	C9	.88(4)	126.(2)
H8	C8	C7		128.(2)
H9	C9	N3'	.94(3)	118.(2)
H9	C9	C8		133.(2)
H10a	C10	H10b	.84(3)	102.(3)
H10a	C10	C11		110.(2)
H10a	C10	Mo		99.(2)
H10b	C10	C11	.88(3)	109.(2)
H10b	C10	Mo		108.(2)
H12a	C12	H12b	.960(4)	109.5(4)
H12a	C12	H12c		109.5(3)
H12a	C12	C11		109.5(4)
H12b	C12	H12c	.960(4)	109.5(5)
H12b	C12	C11		109.5(3)
H12c	C12	C11	.960(4)	109.5(4)
H13a	C13	H13b	.960(3)	109.5(5)
H13a	C13	H13c		109.5(4)
H13a	C13	C11		109.5(3)
H13b	C13	H13c	.960(6)	109.5(4)
H13b	C13	C11		109.5(3)
H13c	C13	C11	.960(4)	109.5(4)
H15	C15	C16	.92(4)	119.(2)
H15	C15	C14		119.(2)
H16	C16	C17	.95(3)	123.(3)
H16	C16	C15		116.(3)
H17	C17	C18	1.06(4)	117.(2)
H17	C17	C16		124.(2)
H18	C18	C19	.90(4)	120.(2)
H18	C18	C17		119.(2)

Table A.12 continued.

H19	C19	C14	.91(3)	118.(3)	
H19	C19	C18		121.(3)	
H22	C22	C23	.97(3)	121.(2)	
H22	C22	C21		117.(2)	
H23	C23	C24	.89(4)	121.(2)	
H23	C23	C22		118.(2)	
H24	C24	C25	.94(3)	116.(2)	
H24	C24	C23		122.(2)	
H26	C26	C27	.86(4)	103.(2)	
H26	C26	C28		112.(2)	
H26	C26	C21		107.(2)	
H27a	C27	H27b	.960(5)	109.5(5)	
H27a	C27	H27c		109.5(5)	
H27a	C27	C26		109.5(4)	
H27b	C27	H27c	.960(6)	109.5(5)	
H27b	C27	C26		109.5(4)	
H27c	C27	C26	.960(5)	109.5(4)	
H28a	C28	H28b	.960(5)	109.5(5)	
H28a	C28	H28c		109.5(5)	
H28a	C28	C26		109.5(5)	
H28b	C28	H28c	.960(6)	109.5(6)	
H28b	C28	C26		109.5(5)	
H28c	C28	C26	.960(6)	109.5(4)	
H29	C29	C30	.90(3)	107.4(14)	
H29	C29	C31		105.(2)	
H29	C29	C25		110.(2)	
H30a	C30	H30b	.960(7)	109.5(6)	
H30a	C30	H30c		109.5(6)	
H30a	C30	C29		109.5(5)	
H30b	C30	H30c	.960(7)	109.5(6)	
H30b	C30	C29		109.5(5)	
H30c	C30	C29	.960(5)	109.5(5)	
H31a	C31	H31b	.960(6)	109.5(8)	
H31a	C31	H31c		109.5(5)	
H31a	C31	C29		109.5(5)	
H31b	C31	H31c	.960(8)	109.5(6)	
H31b	C31	C29		109.5(4)	
	H31c	C31	C29	.960(7)	109.5(7)

Crystallographic Data for [TpMo(O)(NAr)]₂O, 3Table A.13: Crystallographic data.

A. Crystal data (298 K)	3
<i>a</i> , Å	11.419(4)
<i>b</i> , Å	17.597(5)
<i>c</i> , Å	12.32(4)
α, deg.	
β, deg.	98.16(3)
γ, deg.	
<i>V</i> , Å ³	2451(1)
<i>d</i> _{calc} , g cm ⁻³ (298 K)	
Empirical formula	C ₄₂ H ₅₄ N ₁₄ O ₃ B ₂ Mo ₂
Formula wt, g	
Crystal system	Monoclinic
Space group	P 2 ₁ /n
<i>Z</i>	
F(000), electrons	1044
Crystal size (mm ³)	0.36 x 0.1 x 0.08
B. Data collection (298 K)	
Radiation, λ (Å)	Mo-K _α , 0.71073
Mode	ω-scan
Scan range	Symmetrically over 1.2° about K _{α1,2} maximum
Background	offset 1.0 and -1.0 in ω from K _{α1,2} maximum
Scan rate, deg. min. ⁻¹	3 – 6
2θ range, deg.	3 – 45
Range of <i>h k l</i>	$\begin{array}{ccccccc} 0 & \leq & h & \leq & 13 \\ -0 & \leq & k & \leq & 18 \\ -12 & \leq & l & \leq & 12 \end{array}$
Total reflections measured	3402
Unique reflections	3216
Absorption coeff. μ (Mo-K _α), mm ⁻¹	0.56
Min. & Max. Transmission	0.95751 0.94042
C. Structure refinement	
<i>S</i> , Goodness-of-fit	1.5466
Reflections used, <i>I</i> > 2σ(<i>I</i>)	1738
No. of variables	299
<i>R</i> , w <i>R</i> * (%)	6.19, 6.3
<i>R</i> _{int} . (%)	2.39
Max. shift/esd	0.0201

Table A.13 continued.

min. peak in diff. four. map ($\text{e } \text{\AA}^{-3}$)	-0.912
max. peak in diff. four. map ($\text{e } \text{\AA}^{-3}$)	0.457

* Relevant expressions are as follows, where in the footnote F_o and F_c represent, respectively, the observed and calculated structure-factor amplitudes.

Function minimized was $w(|F_o| - |F_c|)^2$, where $w = (\sigma(F))^{-2}$

$$R = \sum(|F_o| - |F_c|) / \sum |F_o|$$

$$wR = [\sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}$$

$$S = [\sum w(|F_o| - |F_c|)^2 / (m-n)]^{1/2}$$

Table A.14: Fractional coordinates and equivalent isotropic^a thermal parameters ($\text{\AA}^2$) for the non-H atoms of compound 3.

Atom	x	y	z	U
Mo	0.16020(9)	0.02776(6)	0.03017(9)	0.0367(3)
N1	0.1558(8)	0.0995(5)	0.1252(8)	0.042(4)
N2	0.1798(14)	0.1127(8)	-0.2016(12)	0.078(7)
N3	0.1094(11)	0.1056(7)	-0.1235(9)	0.051(5)
N4	0.3714(13)	0.0773(7)	-0.0966(14)	0.088(7)
N5	0.3337(10)	0.0717(7)	0.0021(11)	0.067(5)
N6	0.2447(11)	-0.0201(9)	-0.2022(11)	0.085(6)
N7	0.1874(9)	-0.0446(6)	-0.1206(8)	0.052(5)
O1	0.0	0.0	0.0	0.042(4)
O2	0.2229(7)	-0.0468(4)	0.1058(7)	0.058(3)
B	0.288(2)	0.065(2)	-0.202(2)	0.093(11)
C1	0.1760(11)	0.1528(7)	0.2115(11)	0.044(5)
C2	0.2047(12)	0.1275(7)	0.3207(11)	0.054(5)
C3	0.2250(13)	0.1819(10)	0.4031(12)	0.074(7)
C4	0.2230(13)	0.2583(9)	0.3771(14)	0.073(7)
C5	0.1941(13)	0.2811(8)	0.2725(14)	0.075(7)
C6	0.1685(12)	0.2314(8)	0.1863(11)	0.060(6)
C7	0.209(2)	0.0430(9)	0.3476(12)	0.092(8)
C8	0.098(2)	0.0170(12)	0.373(2)	0.21(2)
C9	0.304(2)	0.0221(11)	0.432(2)	0.28(2)
C10	0.133(2)	0.2577(9)	0.075(2)	0.096(9)
C11	0.238(2)	0.2820(11)	0.0203(13)	0.132(12)
C12	0.038(2)	0.3174(10)	0.0594(15)	0.137(11)
C13	0.248(2)	-0.0769(11)	-0.2747(14)	0.109(9)
C14	0.188(2)	-0.1391(10)	-0.2420(14)	0.098(9)
C15	0.1520(12)	-0.1171(8)	-0.1440(12)	0.063(6)
C16	0.484(2)	0.1006(14)	-0.081(2)	0.129(13)
C17	0.514(2)	0.1123(13)	0.027(2)	0.127(13)
C18	0.4221(15)	0.0916(9)	0.079(2)	0.084(8)
C19	0.0172(14)	0.1480(8)	-0.1510(12)	0.061(6)
C20	0.027(2)	0.1858(10)	-0.247(2)	0.098(10)
C21	0.127(2)	0.1619(11)	-0.277(2)	0.105(11)

^aFor anisotropic atoms, the U value is U_{eq} , calculated as $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* A_{ij}$ where A_{ij} is the dot product of the i^{th} and j^{th} direct space unit cell vectors.

Table A.15: Bond Lengths (Å) and Angles (°) for the non-H atoms of compound 3.

<u>1</u>	<u>2</u>	<u>3</u>	<u>1-2</u>	<u>1-2-3</u>
N1	Mo	N3	1.728(9)	95.3(4)
N1	Mo	N5		87.9(5)
N1	Mo	N7		165.6(4)
N1	Mo	O1		101.7(3)
N3	Mo	N5	2.342(11)	78.0(4)
N3	Mo	N7		73.6(4)
N3	Mo	O1		82.5(3)
N3	Mo	O2		158.0(4)
N5	Mo	N7	2.200(12)	80.8(4)
N5	Mo	O1		159.0(3)
N5	Mo	O2		92.2(4)
N7	Mo	O1	2.309(11)	86.3(3)
N7	Mo	O2		85.5(4)
O1	Mo	O2	1.8789(12)	103.3(3)
O2	Mo	N1	1.706(8)	104.0(4)
O1	Mo _a		1.8789(12)	
C1	N1	Mo	1.41(2)	168.1(8)
N3	N2	B	1.34(2)	122.0(15)
B	N2	C21	1.49(3)	130.(2)
C21	N2	N3	1.35(2)	107.(2)
C19	N3	Mo	1.30(2)	130.3(10)
C19	N3	N2		107.8(12)
Mo	N3	N2		121.9(9)
N5	N4	B	1.35(2)	121.(2)
B	N4	C16	1.52(3)	130.(2)
C16	N4	N5	1.34(3)	109.(2)
C18	N5	Mo	1.33(2)	126.3(12)
C18	N5	N4		108.3(13)
Mo	N5	N4		125.2(9)
N7	N6	B	1.35(2)	119.3(15)
B	N6	C13	1.57(3)	132.(2)
C13	N6	N7	1.34(2)	108.6(14)
C15	N7	Mo	1.36(2)	128.3(9)
C15	N7	N6		107.7(12)
Mo	N7	N6		124.1(9)
Mo	O1	Mo _a		180.(0)
N2	B	N4		109.(2)
N2	B	N6		106.(2)
N4	B	N6		107.(2)
C2	C1	C6	1.41(2)	121.0(12)
C2	C1	N1		119.9(11)
C6	C1	N1	1.42(2)	119.1(11)
C3	C2	C7	1.39(2)	121.1(12)
C3	C2	C1		118.0(12)
C7	C2	C1	1.52(2)	120.8(12)

Table A.15 continued.

C4	C3	C2	1.38(2)	120.4(13)
C5	C4	C3	1.35(2)	120.5(15)
C6	C5	C4	1.37(2)	123.1(14)
C10	C6	C1	1.45(2)	121.2(13)
C10	C6	C5		121.8(14)
C1	C6	C5		116.9(13)
C8	C7	C9	1.42(3)	111.(2)
C8	C7	C2		111.(2)
C9	C7	C2	1.44(3)	113.8(14)
C11	C10	C12	1.51(3)	110.4(14)
C11	C10	C6		112.(2)
C12	C10	C6	1.51(2)	116.(2)
C14	C13	N6	1.38(3)	110.(2)
C15	C14	C13	1.38(2)	105.(2)
N7	C15	C14		109.4(14)
C17	C16	N4	1.34(4)	107.(2)
C18	C17	C16	1.35(3)	109.(2)
N5	C18	C17		107.(2)
C20	C19	N3	1.38(2)	110.(2)
C21	C20	C19	1.31(3)	105.(2)
N2	C21	C20		110.(2)

Table A.16: Anisotropic thermal parameters^a for the non-H atoms of compound 3.

Atom	U11	U22	U33	U12	U13	U23
Mo	0.0337(6)	0.0329(6)	0.0432(6)	-0.0037(8)	0.0047(4)	-0.0049(8)
N1	0.039(6)	0.037(6)	0.045(6)	-0.007(5)	-0.013(5)	-0.001(6)
N2	0.115(13)	0.057(10)	0.068(10)	-0.009(9)	0.037(10)	-0.004(8)
N3	0.058(8)	0.056(8)	0.041(7)	-0.001(7)	0.019(7)	0.007(6)
N4	0.070(11)	0.078(10)	0.130(15)	0.003(8)	0.064(11)	0.006(10)
N5	0.047(8)	0.063(8)	0.093(11)	-0.001(7)	0.016(8)	0.001(7)
N6	0.105(10)	0.075(10)	0.089(10)	0.002(10)	0.057(9)	-0.015(11)
N7	0.064(8)	0.048(9)	0.048(7)	-0.007(6)	0.021(6)	-0.007(6)
O1	0.051(7)	0.039(7)	0.039(7)	-0.008(5)	0.014(6)	-0.005(5)
O2	0.060(6)	0.035(6)	0.073(6)	0.006(4)	-0.006(5)	-0.002(4)
B	0.10(2)	0.12(2)	0.07(2)	-0.01(2)	0.053(15)	-0.02(2)
C1	0.049(9)	0.035(8)	0.045(9)	-0.002(7)	-0.008(7)	0.007(7)
C2	0.071(10)	0.039(9)	0.049(9)	-0.018(8)	-0.006(8)	-0.015(8)
C3	0.099(13)	0.078(13)	0.046(10)	-0.024(10)	0.012(9)	-0.008(9)
C4	0.090(13)	0.060(12)	0.069(12)	-0.032(10)	0.009(10)	-0.043(10)
C5	0.093(13)	0.047(10)	0.079(12)	0.001(9)	-0.010(10)	-0.014(10)
C6	0.073(11)	0.060(11)	0.042(9)	0.003(9)	-0.012(8)	-0.001(8)
C7	0.16(2)	0.058(13)	0.052(10)	-0.032(12)	-0.020(11)	0.000(8)
C8	0.22(3)	0.10(2)	0.30(4)	-0.04(2)	0.04(3)	0.05(2)
C9	0.40(5)	0.09(2)	0.27(3)	0.03(3)	-0.18(3)	0.02(2)
C10	0.16(2)	0.034(10)	0.086(14)	-0.017(11)	-0.010(13)	0.004(9)
C11	0.24(3)	0.09(2)	0.063(13)	0.04(2)	0.014(15)	0.028(11)
C12	0.14(2)	0.075(14)	0.17(2)	0.011(13)	-0.06(2)	0.036(13)
C13	0.18(2)	0.084(14)	0.089(14)	-0.003(14)	0.091(13)	-0.030(12)
C14	0.15(2)	0.063(12)	0.094(14)	0.005(12)	0.061(13)	-0.025(11)
C15	0.072(11)	0.036(9)	0.080(12)	0.005(8)	0.013(9)	-0.027(9)
C16	0.10(2)	0.13(2)	0.19(3)	0.02(2)	0.11(2)	-0.02(2)
C17	0.057(14)	0.10(2)	0.24(3)	-0.029(12)	0.05(2)	-0.02(2)
C18	0.042(10)	0.067(12)	0.14(2)	0.001(9)	0.006(12)	0.004(12)
C19	0.076(12)	0.044(9)	0.058(11)	-0.008(9)	-0.012(9)	0.007(8)
C20	0.14(2)	0.067(13)	0.075(15)	0.002(13)	-0.023(13)	0.006(11)
C21	0.20(3)	0.057(13)	0.077(15)	-0.018(15)	0.07(2)	0.016(11)

^a U_{ij} are the mean-square amplitudes of vibration in Å² from the general temperature

factor expression $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$

Table A.17: Fractional coordinates and isotropic thermal parameters ($\text{\AA}^2$) for the H atoms of compound **3**.

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>	<u>U</u>
H	0.317(10)	0.068(6)	-0.286(9)	0.07(4)
H3	0.24035	0.16639	0.47844	0.08
H4	0.24265	0.29533	0.43391	0.08
H5	0.19123	0.33467	0.25727	0.08
H7	0.22473	0.01775	0.28224	0.08
H8a	0.0361	0.0318	0.31595	0.08
H8b	0.08328	0.03909	0.44135	0.08
H8c	0.09928	-0.03734	0.37974	0.08
H9a	0.37764	0.04036	0.4122	0.08
H9b	0.30727	-0.032220	0.43863	0.08
H9c	0.29127	0.0442	0.50024	0.08
H10	0.09764	0.2133	0.03916	0.08
H11a	0.2105	0.29888	-0.05299	0.08
H11b	0.29061	0.23969	0.01789	0.08
H11c	0.27897	0.32269	0.06131	0.08
H12a	-0.02781	0.30124	0.09448	0.08
H12b	0.01206	0.32454	-0.01751	0.08
H12c	0.06848	0.36438	0.09128	0.08
H13	0.28566	-0.07446	-0.33929	0.08
H14	0.17437	-0.18693	-0.27914	0.08
H15	0.10875	-0.1483	-0.09963	0.08
H16	0.53389	0.10772	-0.13686	0.08
H17	0.58833	0.132	0.06137	0.08
H18	0.42095	0.09132	0.15645	0.08
H19	-0.04801	0.15239	-0.11009	0.08
H20	-0.02805	0.22167	-0.28494	0.08
H21	0.15702	0.17755	-0.34224	0.08

Table A.18: Bond Lengths (Å) and Angles (°) of the H atoms of compound 3.

<u>1</u>	<u>2</u>	<u>3</u>	<u>1-2</u>	<u>1-2-3</u>
H	B	N2	1.13(12)	109.(6)
H	B	N4		123.(6)
H	B	N6		100.(6)
H3	C3	C4	0.960(14)	120.(2)
H3	C3	C2		120.(2)
H4	C4	C5	0.96(2)	120.(2)
H4	C4	C3		120.(2)
H5	C5	C6	0.960(15)	118.(2)
H5	C5	C4		118.(2)
H7	C7	C8	0.96(2)	109.(2)
H7	C7	C9		106.(2)
H7	C7	C2		105.9(13)
H8a	C8	H8b	0.96(2)	109.(2)
H8a	C8	H8c		109.(2)
H8a	C8	C7		109.(2)
H8b	C8	H8c	0.96(2)	109.(2)
H8b	C8	C7		109.(2)
H8c	C8	C7	0.96(2)	109.(2)
H9a	C9	H9b	0.96(3)	109.(2)
H9a	C9	H9c		109.(2)
H9a	C9	C7		109.(2)
H9b	C9	H9c	0.96(2)	109.(2)
H9b	C9	C7		109.(2)
H9c	C9	C7	0.96(2)	110.(2)
H10	C10	C11	0.96(2)	109.(2)
H10	C10	C12		105.(2)
H10	C10	C6		102.6(14)
H11a	C11	H11b	0.96(2)	109.(2)
H11a	C11	H11c		109.(2)
H11a	C11	C10		109.(2)
H11b	C11	H11c	0.96(2)	109.(2)
H11b	C11	C10		109.(2)
H11c	C11	C10	0.96(2)	109.(2)
H12a	C12	H12b	0.96(2)	109.(2)
H12a	C12	H12c		109.(2)
H12a	C12	C10		109.(2)
H12b	C12	H12c	0.96(2)	109.(2)
H12b	C12	C10		109.(2)
H12c	C12	C10	0.96(2)	109.5(15)
H13	C13	C14	0.96(2)	125.(2)
H13	C13	N6		125.(2)
H14	C14	C15	0.96(2)	128.(2)
H14	C14	C13		127.(2)
H15	C15	N7	0.960(15)	125.4(15)
H15	C15	C14		125.2(14)
H16	C16	C17	0.96(3)	126.(2)

Table A.18 continued.

H16	C16	N4		127.(2)
H17	C17	C18	0.96(2)	126.(3)
H17	C17	C16		126.(3)
H18	C18	N5	0.96(2)	126.(2)
H18	C18	C17		127.(2)
H19	C19	C20	0.96(2)	125.(2)
H19	C19	N3		124.8(14)
H20	C20	C21	0.96(2)	128.(2)
H20	C20	C19		127.(2)
H21	C21	N2	0.96(2)	125.(2)
		H21	C21	C20
		125.(2)		

Crystallographic Data for 4 and 5.Table A.19: Crystallographic data.

A. Crystal data (298 K)	4	5
a , Å	12.620(2)	10.624(2)
b , Å	13.492(2)	11.766(3)
c , Å	19.682(2)	13.980(3)
α , deg.		86.96(2)
β , deg.		86.54(2)
γ , deg.		67.77(2)
V , Å ³	3351.3(7)	1635.8(7)
d_{calc} , g cm ⁻³ (298 K)	1.283	1.315
Empirical formula	C ₃₂ H ₄₂ BN ₇ OMo	C ₃₂ H ₄₂ BN ₇ OMo
Formula wt, g	647.48	647.48
Crystal system	Orthorhombic	Triclinic
Space group	P2 ₁ 2 ₁ 2 ₁	P $\bar{1}$
Z	4	2
$F(000)$, electrons	1352	676
Crystal size (mm ³)	0.44 x 0.15 x 0.15	0.34 x 0.25 x 0.11
B. Data collection (298 K)		
Radiation, λ (Å)	Mo-K α , 0.71073	
Mode	ω -scan	
Scan range	Symmetrically over 1.2° about K $\alpha_{1,2}$ maximum	
Background	offset 1.0 and -1.0 in ω from K $\alpha_{1,2}$ maximum	
Scan rate, deg. min. ⁻¹	3 – 6	3 – 6
2 θ range, deg.	3 – 55	3 – 55
Range of $h\ k\ l$	0 $\leq h \leq$ 16 0 $\leq k \leq$ 17 0 $\leq l \leq$ 25	0 $\leq h \leq$ 12 -13 $\leq k \leq$ 13 -16 $\leq l \leq$ 16
Total reflections measured	4317	6094
Unique reflections	4288	5755
Absorption coeff. μ (Mo-K α), mm ⁻¹	0.43	0.44
Min. & Max. Transmission	0.928 & 0.950	0.850 & 0.948
C. Structure refinement		
S , Goodness-of-fit	1.56	1.34
Reflections used	2298, $I > 3\sigma(I)$	4596, $I > 2\sigma(I)$
No. of variables	352	463

Supplementary Table 1 continued.

R, wR* (%)	6.00, 5.89	4.84, 4.87
R _{int.} (%)	0.00	2.24
Max. shift/esd	0.001	0.001

Supplementary Table 1 continued.

min. peak in diff. four. map (e Å ⁻³)	-0.66	-0.67
max. peak in diff. four. map (e Å ⁻³)	0.64	0.47

* Relevant expressions are as follows, where in the footnote F_o and F_c represent, respectively, the observed and calculated structure-factor amplitudes.

Function minimized was $w(|F_o| - |F_c|)^2$, where $w = (\sigma(F))^{-2}$

$$R = \sum(|F_o| - |F_c|) / \sum |F_o|$$

$$wR = [\sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}$$

$$S = [\sum w(|F_o| - |F_c|)^2 / (m-n)]^{1/2}$$

Table A.20: Fractional coordinates and equivalent isotropic^a thermal parameters ($\text{\AA}^2$) for the non-H atoms of compound 4.

Atom	x	y	z	U
Mo	0.38168(8)	0.95336(7)	0.35907(5)	0.0408(3)
O1	0.4455(6)	1.0699(5)	0.4022(4)	0.055(3)
N1	0.2483(7)	0.9862(6)	0.3612(5)	0.049(3)
N2	0.3733(9)	0.8293(6)	0.2843(4)	0.042(3)
N3	0.4306(7)	0.8260(7)	0.2250(5)	0.043(3)
N4	0.5582(8)	0.9199(7)	0.3336(5)	0.049(4)
N5	0.5958(8)	0.9067(6)	0.2690(5)	0.042(3)
N6	0.4048(7)	1.0395(7)	0.2596(4)	0.042(3)
N7	0.4606(7)	1.0051(7)	0.2057(4)	0.042(3)
B	0.5158(11)	0.9041(11)	0.2090(7)	0.043(5)
C11	0.1481(9)	1.0289(7)	0.3587(7)	0.052(4)
C12	0.0756(12)	0.9985(10)	0.3097(7)	0.061(5)
C13	-0.0213(12)	1.0449(14)	0.3077(8)	0.087(6)
C14	-0.0456(14)	1.1189(13)	0.3515(11)	0.102(8)
C15	0.027(2)	1.1496(11)	0.3993(8)	0.088(7)
C16	0.1276(13)	1.1079(8)	0.4044(7)	0.065(5)
C17	0.1007(13)	0.9153(12)	0.2624(7)	0.083(6)
C18	0.113(2)	0.942(2)	0.1917(8)	0.199(14)
C19	0.029(2)	0.8323(13)	0.2702(11)	0.159(12)
C20	0.2030(13)	1.1446(12)	0.4555(8)	0.083(7)
C21	0.1561(13)	1.1495(12)	0.5265(7)	0.107(8)
C22	0.248(2)	1.2434(11)	0.4357(10)	0.137(10)
C23	0.3208(11)	0.7432(9)	0.2860(7)	0.057(5)
C24	0.3398(10)	0.6852(10)	0.2332(7)	0.057(5)
C25	0.4123(11)	0.7379(9)	0.1944(6)	0.056(5)
C26	0.6449(9)	0.9177(8)	0.3724(6)	0.053(4)
C27	0.7347(11)	0.9056(10)	0.3355(7)	0.062(5)
C28	0.6999(10)	0.8972(8)	0.2697(8)	0.053(5)
C29	0.3685(10)	1.1282(8)	0.2419(6)	0.051(4)
C30	0.4030(11)	1.1548(9)	0.1778(6)	0.055(5)
C31	0.4612(9)	1.0754(8)	0.1574(6)	0.050(4)
C32	0.4851(11)	1.0819(10)	0.4666(7)	0.081(6)
C1	0.3915(11)	0.8580(8)	0.4341(5)	0.052(4)
C4	0.3162(12)	0.8165(10)	0.4902(6)	0.065(5)
C2	0.346(2)	0.8606(14)	0.5584(9)	0.069(6)
C3	0.1932(15)	0.8515(14)	0.4810(10)	0.064(6)
C5	0.3198(12)	0.7056(8)	0.4875(8)	0.053(6)
C6	0.2454(12)	0.6455(8)	0.4551(8)	0.078(7)
C7	0.2597(12)	0.5430(8)	0.4533(8)	0.085(7)
C8	0.3486(12)	0.5006(8)	0.4838(8)	0.089(7)
C9	0.4230(12)	0.5607(8)	0.5162(8)	0.082(7)
C10	0.4087(12)	0.6631(8)	0.5181(8)	0.065(6)
C2'	0.250(3)	0.879(3)	0.512(2)	0.063(13)
C3'	0.409(3)	0.805(3)	0.556(2)	0.054(12)
C5'	0.287(2)	0.711(2)	0.471(2)	0.041(10)

Table A.20 continued.

C6'	0.191(2)	0.706(2)	0.437(2)	0.061(12)
C7'	0.152(2)	0.615(2)	0.415(2)	0.10(2)
C8'	0.209(2)	0.528(2)	0.428(2)	0.11(2)
C9'	0.306(2)	0.533(2)	0.462(2)	0.059(12)
C10'	0.345(2)	0.625(2)	0.484(2)	0.10(2)

^aFor anisotropic atoms, the U value is U_{eq} , calculated as $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* A_{ij}$ where A_{ij} is the dot product of the i^{th} and j^{th} direct space unit cell vectors.

Table A.21: Bond Lengths (Å) and Angles (°) for the non-H atoms of compound 4.

1	2	3	1-2	1-2-3
O1	Mo	N1	1.960(7)	100.6(4)
O1	Mo	N2		155.1(4)
O1	Mo	N4		81.7(3)
O1	Mo	N6		84.9(3)
N1	Mo	N2	1.741(9)	99.2(4)
N1	Mo	N4		168.5(4)
N1	Mo	N6		90.9(4)
N1	Mo	C1		102.1(5)
N2	Mo	N4	2.232(8)	76.0(4)
N2	Mo	N6		79.8(3)
N2	Mo	C1		90.5(4)
N4	Mo	N6	2.327(10)	78.0(3)
N4	Mo	C1		88.5(5)
N6	Mo	C1	2.295(8)	165.0(4)
C1	Mo	O1	1.963(10)	100.0(4)
C32	O1	Mo	1.37(2)	130.1(7)
C11	N1	Mo	1.390(14)	169.7(8)
N3	N2	C23	1.374(13)	104.7(9)
N3	N2	Mo		124.1(7)
C23	N2	Mo	1.338(15)	131.2(8)
B	N3	C25	1.54(2)	129.1(10)
B	N3	N2		121.2(9)
C25	N3	N2	1.35(2)	108.5(9)
N5	N4	C26	1.369(13)	104.1(9)
N5	N4	Mo		123.9(7)
C26	N4	Mo	1.335(15)	131.8(7)
B	N5	C28	1.55(2)	130.7(11)
B	N5	N4		118.9(9)
C28	N5	N4	1.32(2)	110.4(10)
N7	N6	C29	1.355(12)	106.4(8)
N7	N6	Mo		124.1(7)
C29	N6	Mo	1.329(14)	129.5(7)
B	N7	C31	1.53(2)	130.9(10)
B	N7	N6		120.5(9)
C31	N7	N6	1.344(14)	108.4(9)
N3	B	N5		108.3(9)
N3	B	N7		107.5(10)
N5	B	N7		108.0(9)
C12	C11	C16	1.39(2)	122.8(12)
C12	C11	N1		120.0(11)
C16	C11	N1	1.42(2)	117.0(11)
C13	C12	C17	1.38(2)	120.9(13)
C13	C12	C11		118.1(13)
C17	C12	C11	1.49(2)	121.0(12)
C14	C13	C12	1.35(3)	121.3(15)

Table A.21 continued.

C15	C14	C13	1.37(3)	121.(2)
C16	C15	C14	1.40(2)	122.1(15)
C20	C16	C11	1.47(2)	124.7(13)
C20	C16	C15		120.3(13)
C11	C16	C15		115.0(13)
C18	C17	C19	1.45(2)	111.(2)
C18	C17	C12		115.7(15)
C19	C17	C12	1.45(2)	112.4(14)
C21	C20	C22	1.52(2)	110.3(14)
C21	C20	C16		113.1(13)
C22	C20	C16	1.50(2)	111.4(13)
C24	C23	N2	1.32(2)	113.8(12)
C25	C24	C23	1.39(2)	104.4(11)
N3	C25	C24		108.5(11)
C27	C26	N4	1.36(2)	112.4(11)
C28	C27	C26	1.37(2)	104.4(12)
N5	C28	C27		108.6(12)
C30	C29	N6	1.38(2)	111.4(10)
C31	C30	C29	1.36(2)	103.6(10)
N7	C31	C30		110.1(10)
C4	C1	Mo	1.56(2)	136.8(10)
C2	C4	C3	1.52(2)	102.9(13)
C2	C4	C5		114.6(12)
C2	C4	C1		109.5(12)
C3	C4	C5	1.63(2)	108.3(12)
C3	C4	C1		113.3(11)
C5	C4	C1	1.50(2)	108.3(11)
C6	C5	C10	1.39(2)	120.0(10)
C6	C5	C4		125.2(12)
C10	C5	C4	1.39(2)	114.7(11)
C7	C6	C5	1.395(14)	120.0(13)
C8	C7	C6	1.40(2)	120.0(12)
C9	C8	C7	1.39(2)	120.0(10)
C10	C9	C8	1.395(14)	120.0(13)
C5	C10	C9		120.0(12)
C2'	C4	C3'	1.26(5)	104.(2)
C2'	C4	C5'		123.(3)
C2'	C4	C1		114.(2)
C3'	C4	C5'	1.75(4)	105.(2)
C3'	C4	C1		99.(2)
C5'	C4	C1	1.52(3)	108.0(15)
C6'	C5'	C10'	1.39(4)	120.(2)
C6'	C5'	C4		112.(2)
C10'	C5'	C4	1.40(4)	128.(3)
C7'	C6'	C5'	1.40(4)	120.(2)
C8'	C7'	C6'	1.40(4)	120.(3)
C9'	C8'	C7'	1.39(4)	120.(2)
C10'	C9'	C8'	1.39(4)	120.(2)
C5'	C10'	C9'		120.(3)

Table A.22: Anisotropic thermal parameters^a for the non-H atoms of compound 4.

Atom	U11	U22	U33	U12	U13	U23
Mo	0.0503(5)	0.0369(4)	0.0352(4)	-0.0051(6)	0.0050(6)	-0.0042(6)
O1	0.077(6)	0.045(5)	0.044(4)	-0.012(4)	-0.001(4)	-0.014(4)
N1	0.058(6)	0.042(5)	0.047(5)	-0.006(4)	0.009(6)	-0.003(6)
N2	0.049(6)	0.035(5)	0.041(5)	-0.008(6)	-0.005(6)	0.000(4)
N3	0.049(6)	0.036(5)	0.044(5)	0.002(5)	-0.003(5)	-0.009(5)
N4	0.054(6)	0.045(6)	0.046(6)	-0.004(5)	-0.001(5)	0.006(4)
N5	0.048(7)	0.034(5)	0.044(6)	-0.008(5)	0.009(5)	0.004(4)
N6	0.043(6)	0.042(5)	0.042(5)	0.009(6)	-0.001(4)	-0.012(5)
N7	0.045(6)	0.048(5)	0.033(5)	-0.002(5)	-0.002(5)	0.010(5)
B	0.041(8)	0.053(8)	0.034(7)	0.015(7)	0.002(7)	0.002(7)
C11	0.063(8)	0.037(6)	0.055(6)	0.006(6)	0.016(8)	0.017(7)
C12	0.060(10)	0.067(8)	0.056(8)	0.011(7)	0.001(7)	0.006(7)
C13	0.076(11)	0.080(10)	0.104(12)	-0.023(12)	-0.033(9)	-0.001(12)
C14	0.094(13)	0.079(12)	0.13(2)	0.042(10)	-0.013(13)	0.029(13)
C15	0.13(2)	0.055(9)	0.078(11)	0.029(11)	0.013(12)	0.001(9)
C16	0.069(10)	0.031(6)	0.094(10)	0.002(8)	0.013(10)	0.003(7)
C17	0.061(10)	0.113(12)	0.074(10)	-0.020(10)	-0.020(9)	-0.030(9)
C18	0.27(3)	0.22(2)	0.099(14)	-0.05(3)	0.06(2)	-0.05(2)
C19	0.16(2)	0.12(2)	0.20(3)	-0.00(2)	0.08(2)	-0.09(2)
C20	0.084(12)	0.077(11)	0.087(11)	0.009(9)	0.008(10)	-0.025(10)
C21	0.14(2)	0.100(13)	0.078(10)	0.035(12)	-0.000(11)	-0.022(10)
C22	0.20(2)	0.081(13)	0.13(2)	-0.011(15)	-0.02(2)	-0.013(13)
C23	0.067(9)	0.043(7)	0.061(8)	-0.012(7)	-0.003(7)	-0.009(7)
C24	0.059(10)	0.054(8)	0.058(8)	-0.014(7)	-0.019(7)	0.008(7)
C25	0.070(11)	0.049(7)	0.048(7)	0.020(7)	-0.025(7)	-0.011(6)
C26	0.043(8)	0.064(8)	0.050(7)	-0.012(6)	-0.012(6)	0.006(6)
C27	0.047(8)	0.073(9)	0.066(10)	-0.015(7)	-0.012(7)	-0.004(7)
C28	0.033(8)	0.041(7)	0.086(11)	0.003(6)	-0.003(7)	-0.002(7)
C29	0.058(8)	0.040(6)	0.054(7)	0.013(7)	-0.005(7)	-0.002(6)
C30	0.073(10)	0.049(7)	0.044(7)	-0.001(8)	-0.013(7)	0.013(6)
C31	0.059(8)	0.052(8)	0.040(7)	-0.005(6)	-0.002(6)	0.009(5)
C32	0.086(11)	0.070(10)	0.087(11)	-0.015(8)	-0.010(9)	-0.006(8)
C1	0.064(8)	0.041(6)	0.049(6)	-0.022(7)	-0.002(8)	-0.005(5)
C4	0.082(10)	0.055(8)	0.057(8)	-0.007(8)	0.012(8)	0.001(7)

^a U_{ij} are the mean-square amplitudes of vibration in Å² from the general temperature

factor expression $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^{*}b^{*}U_{12} + 2hla^{*}c^{*}U_{13} + 2klb^{*}c^{*}U_{23})]$

Table A.23: Fractional coordinates and isotropic thermal parameters ($\text{\AA}^2$) for the H atoms of compound 4.

Atom	x	y	z	U
H	0.553(7)	0.892(7)	0.162(5)	0.05(3)
H1	0.46089	0.82928	0.43170	0.08
H13	-0.07278	1.024550	0.27462	0.08
H14	-0.11388	1.15008	0.34912	0.08
H15	0.00692	1.20148	0.43028	0.08
H17	0.17014	0.89479	0.27646	0.08
H18a	0.16124	0.99732	0.1881	0.08
H18b	0.04577	0.96051	0.17312	0.08
H18c	0.14138	0.88689	0.16688	0.08
H19a	0.02194	0.81621	0.31755	0.08
H19b	0.0559	0.77599	0.24608	0.08
H19c	-0.03971	0.84961	0.25231	0.08
H20	0.25946	1.09687	0.45679	0.08
H21a	0.1278	1.08583	0.53853	0.08
H21b	0.10056	1.19803	0.52745	0.08
H21c	0.2104	1.16768	0.55829	0.08
H22a	0.29651	1.26532	0.46988	0.08
H22b	0.19115	1.29065	0.43143	0.08
H22c	0.28393	1.23753	0.39297	0.08
H23	0.27368	0.72511	0.32221	0.08
H24	0.31026	0.62106	0.22382	0.08
H25	0.4441	0.71566	0.1528	0.08
H26	0.64393	0.92401	0.42096	0.08
H27	0.80637	0.90343	0.35165	0.08
H28	0.74391	0.88626	0.23061	0.08
H29	0.32388	1.16874	0.27004	0.08
H30	0.38917	1.21511	0.15349	0.08
H31	0.49733	1.07025	0.11462	0.08
H32a	0.51086	1.14837	0.4719	0.08
H32b	0.54202	1.03594	0.47388	0.08
H32c	0.42992	1.06975	0.4992	0.08
H2a	0.41875	0.86334	0.57297	0.08
H2b	0.31618	0.92593	0.55962	0.08
H2c	0.30695	0.81775	0.58809	0.08
H3a	0.14824	0.82633	0.516310	0.08
H3b	0.18663	0.92228	0.47876	0.08
H3c	0.17256	0.8231	0.43825	0.08
H6	0.18422	0.67468	0.43409	0.08
H7	0.20848	0.50168	0.431	0.08
H8	0.35845	0.43007	0.48258	0.08
H9	0.48417	0.53146	0.53724	0.08
H10	0.45989	0.70447	0.54033	0.08
H2'a	0.19661	0.86192	0.47969	0.08
H2'b	0.22378	0.86803	0.5573	0.08
H2'c	0.26955	0.94718	0.506920	0.08
H3'a	0.3773	0.79067	0.59935	0.08

Table A.23 continued.

H3'b	0.46266	0.75723	0.54623	0.08
H3'c	0.44013	0.87027	0.55761	0.08
H6'	0.15093	0.76536	0.42789	0.08
H7'	0.08536	0.61097	0.39115	0.08
H8'	0.18257	0.46531	0.41264	0.08
H9'	0.3453	0.47402	0.47091	0.08
H10'	0.41087	0.62842	0.507620	0.08

Table A.24: Bond Lengths (Å) and Angles (°) of the H atoms of compound 4.

<u>1</u>	<u>2</u>	<u>3</u>	<u>1-2</u>	<u>1-2-3</u>
H	B	N3	1.06(9)	113.(5)
H	B	N5		112.(5)
H	B	N7		107.(5)
H1	C1	Mo	0.96(2)	111.6(2)
H1	C1	C4		111.6(2)
H13	C13	C14	0.96(2)	119.(2)
H13	C13	C12		119.(2)
H14	C14	C15	0.96(2)	120.(2)
H14	C14	C13		120.(2)
H15	C15	C16	0.96(2)	119.(2)
H15	C15	C14		119.(2)
H17	C17	C18	0.96(2)	104.(2)
H17	C17	C19		109.(2)
H17	C17	C12		103.4(13)
H18a	C18	H18b	0.96(2)	109.(2)
H18a	C18	H18c		109.(2)
H18a	C18	C17		110.(2)
H18b	C18	H18c	0.96(2)	109.(2)
H18b	C18	C17		109.(2)
H18c	C18	C17	0.96(2)	109.(2)
H19a	C19	H19b	0.96(2)	109.(2)
H19a	C19	H19c		109.(2)
H19a	C19	C17		109.(2)
H19b	C19	H19c	0.96(2)	109.(2)
H19b	C19	C17		109.(2)
H19c	C19	C17	0.96(2)	110.(2)
H20	C20	C21	0.96(2)	107.1(14)
H20	C20	C22		108.9(15)
H20	C20	C16		105.8(14)
H21a	C21	H21b	0.96(2)	109.(2)
H21a	C21	H21c		109.5(15)
H21a	C21	C20		109.5(14)
H21b	C21	H21c	0.96(2)	109.(2)
H21b	C21	C20		109.5(13)
H21c	C21	C20	0.96(2)	109.5(15)
H22a	C22	H22b	0.96(2)	109.(2)
H22a	C22	H22c		109.(2)
H22a	C22	C20		109.(2)
H22b	C22	H22c	0.96(2)	109.(2)
H22b	C22	C20		110.(2)
H22c	C22	C20	0.96(2)	109.5(14)
H23	C23	C24	0.960(13)	123.1(12)
H23	C23	N2		123.1(12)
H24	C24	C25	0.960(13)	127.8(13)
H24	C24	C23		127.8(13)
H25	C25	N3	0.960(13)	125.7(12)
H25	C25	C24		125.7(12)
H26	C26	C27	0.960(12)	123.8(11)

Table A.24 continued.

H26	C26	N4		123.8(11)
H27	C27	C28	0.960(14)	127.8(13)
H27	C27	C26		127.8(13)
H28	C28	N5	0.960(14)	125.7(14)
H28	C28	C27		125.7(13)
H29	C29	C30	0.960(12)	124.3(11)
H29	C29	N6		124.3(10)
H30	C30	C31	0.960(12)	128.2(12)
H30	C30	C29		128.2(12)
H31	C31	N7	0.960(11)	124.9(11)
H31	C31	C30		125.0(11)
H32a	C32	H32b	0.960(13)	109.5(14)
H32a	C32	H32c		109.5(13)
H32a	C32	O1		109.5(12)
H32b	C32	H32c	0.960(14)	109.5(13)
H32b	C32	O1		109.5(12)
H32c	C32	O1	0.960(14)	109.5(12)
H2a	C2	H2b	0.96(2)	109.(2)
H2a	C2	H2c		109.(2)
H2a	C2	C4		121.(2)
H2b	C2	H2c	0.96(2)	109.(2)
H2b	C2	C4		106.(2)
H2c	C2	C4	0.96(2)	100.(2)
H3a	C3	H3b	0.96(2)	109.(2)
H3a	C3	H3c		109.(2)
H3a	C3	C4		112.(2)
H3b	C3	H3c	0.96(2)	109.(2)
H3b	C3	C4		112.(2)
H3c	C3	C4	0.96(2)	104.(2)
H6	C6	C7	0.960(14)	120.0(13)
H6	C6	C5		120.0(10)
H7	C7	C8	0.960(13)	120.0(10)
H7	C7	C6		120.0(14)
H8	C8	C9	0.960(10)	120.0(14)
H8	C8	C7		120.0(13)
H9	C9	C10	0.960(14)	120.0(13)
H9	C9	C8		120.0(10)
H10	C10	C5	0.960(13)	120.0(10)
H10	C10	C9		120.0(14)
H2'a	C2'	H2'b	0.96(4)	109.(4)
H2'a	C2'	H2'c		109.(4)
H2'a	C2'	C4		95.(3)
H2'b	C2'	H2'c	0.96(4)	109.(4)
H2'b	C2'	C4		117.(4)
H2'c	C2'	C4	0.96(4)	116.(4)
H3'a	C3'	H3'b	0.96(4)	109.(4)
H3'a	C3'	H3'c		109.(4)
H3'a	C3'	C4		113.(3)
H3'b	C3'	H3'c	0.96(4)	109.(4)

Table A.24 continued.

H3'b	C3'	C4		112.(3)
H3'c	C3'	C4	0.96(4)	103.(3)
H6'	C6'	C7'	0.96(3)	120.(3)
H6'	C6'	C5'		120.(2)
H7'	C7'	C8'	0.96(3)	120.(2)
H7'	C7'	C6'		120.(3)
H8'	C8'	C9'	0.96(3)	120.(3)
H8'	C8'	C7'		120.(3)
H9'	C9'	C10'	0.96(3)	120.(3)
H9'	C9'	C8'		120.(2)
H10'	C10'	C5'	0.96(3)	120.(2)
H10'	C10'	C9'		120.(3)

Table 25: Fractional coordinates and equivalent isotropic^a thermal parameters (Å²) for the non-H atoms of compound 5.

Atom	x	y	z	U
Mo	0.25571(4)	0.14529(3)	0.23974(3)	0.02951(13)
O1	0.4338(3)	0.1543(3)	0.2327(2)	0.0427(12)
N1	0.1497(3)	0.2966(3)	0.1754(3)	0.0328(14)
N2	0.1026(3)	0.0567(3)	0.2267(2)	0.0334(13)
N3	0.1241(4)	-0.0406(3)	0.1712(3)	0.0407(15)
N4	0.3664(3)	-0.0550(3)	0.2681(3)	0.0397(14)
N5	0.3645(4)	-0.1398(3)	0.2060(3)	0.0408(15)
N6	0.3021(4)	0.0860(3)	0.0771(3)	0.0391(15)
N7	0.3009(4)	-0.0230(3)	0.0504(3)	0.0398(15)
B	0.2631(6)	-0.1069(5)	0.1243(4)	0.045(2)
C1	0.2030(4)	0.1884(4)	0.3587(3)	0.035(2)
C2	0.2391(6)	0.1188(5)	0.5263(3)	0.063(2)
C3	0.1776(6)	0.3385(5)	0.4847(3)	0.056(2)
C4	0.1541(5)	0.2212(4)	0.4607(3)	0.043(2)
C5	0.0040(5)	0.2406(4)	0.4707(3)	0.043(2)
C6	-0.0472(7)	0.1667(6)	0.5294(4)	0.063(3)
C7	-0.1827(9)	0.1855(8)	0.5345(6)	0.084(4)
C8	-0.2695(9)	0.2756(10)	0.4832(6)	0.091(4)
C9	-0.2205(7)	0.3513(7)	0.4242(5)	0.077(3)
C10	-0.0855(6)	0.3330(5)	0.4195(4)	0.054(2)
C11	0.0628(4)	0.4157(4)	0.1957(3)	0.032(2)
C12	-0.0722(4)	0.4537(4)	0.1689(3)	0.037(2)
C13	-0.1535(5)	0.5720(5)	0.1882(4)	0.050(2)
C14	-0.1056(6)	0.6499(5)	0.2310(4)	0.058(2)
C15	0.0255(6)	0.6126(5)	0.2557(4)	0.050(2)
C16	0.1135(5)	0.4961(4)	0.2373(3)	0.037(2)
C17	-0.1223(5)	0.3683(5)	0.1189(4)	0.046(2)
C18	-0.0861(6)	0.3680(6)	0.0118(4)	0.070(3)
C19	-0.2724(5)	0.3912(6)	0.1351(5)	0.081(3)
C20	0.2616(5)	0.4601(5)	0.2558(4)	0.045(2)
C21	0.3449(5)	0.4549(5)	0.1618(4)	0.061(2)
C22	0.2953(6)	0.5389(5)	0.3267(4)	0.070(3)
C23	-0.0243(5)	0.0860(5)	0.2612(3)	0.041(2)
C24	-0.0846(5)	0.0102(5)	0.2285(4)	0.050(2)
C25	0.0123(5)	-0.0690(5)	0.1720(4)	0.049(2)
C26	0.4600(5)	-0.1120(5)	0.3296(4)	0.048(2)
C27	0.5189(6)	-0.2321(5)	0.3088(5)	0.058(2)
C28	0.4561(5)	-0.2465(5)	0.2304(4)	0.052(2)
C29	0.3360(5)	0.1392(5)	-0.0025(3)	0.046(2)
C30	0.3583(5)	0.0655(5)	-0.0801(4)	0.053(2)
C31	0.3359(5)	-0.0357(6)	-0.0441(4)	0.053(2)
C32	0.5146(5)	0.1679(5)	0.3034(4)	0.062(2)

^aFor anisotropic atoms, the U value is U_{eq} , calculated as $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* A_{ij}$ where A_{ij} is the dot product of the i^{th} and j^{th} direct space unit cell vectors.

Table A.26: Bond Lengths (Å) and Angles (°) for the non-H atoms of compound 5.

1	2	3	1-2	1-2-3
O1	Mo	N1	1.928(3)	102.9(2)
O1	Mo	N2		155.46(12)
O1	Mo	N4		83.56(14)
O1	Mo	N6		85.36(14)
N1	Mo	N2	1.952(3)	94.2(2)
N1	Mo	N4		160.7(2)
N1	Mo	N6		80.48(14)
N1	Mo	C1		97.6(2)
N2	Mo	N4	2.235(4)	74.87(13)
N2	Mo	N6		80.24(14)
N2	Mo	C1		93.7(2)
N4	Mo	N6	2.265(3)	81.95(12)
N4	Mo	C1		99.0(2)
N6	Mo	C1	2.386(4)	173.5(2)
C1	Mo	O1	1.765(4)	101.2(2)
C32	O1	Mo	1.398(7)	131.7(3)
C11	N1	Mo	1.419(5)	141.1(3)
N3	N2	C23	1.363(5)	105.6(4)
N3	N2	Mo		122.9(3)
C23	N2	Mo	1.336(6)	131.4(3)
B	N3	C25	1.536(6)	128.9(4)
B	N3	N2		121.3(4)
C25	N3	N2	1.339(7)	109.7(4)
N5	N4	C26	1.363(6)	106.2(4)
N5	N4	Mo		121.6(2)
C26	N4	Mo	1.326(6)	131.0(4)
B	N5	C28	1.558(7)	129.7(4)
B	N5	N4		121.1(3)
C28	N5	N4	1.338(5)	109.1(4)
N7	N6	C29	1.359(6)	105.9(4)
N7	N6	Mo		121.3(3)
C29	N6	Mo	1.339(6)	132.9(3)
B	N7	C31	1.524(7)	131.2(5)
B	N7	N6		119.7(4)
C31	N7	N6	1.352(6)	109.2(4)
N3	B	N5		106.5(4)
N3	B	N7		109.9(4)
N5	B	N7		109.0(5)
C4	C1	Mo	1.510(6)	177.2(4)
C4	C2		1.530(6)	
C4	C3		1.543(8)	
C5	C4	C1	1.529(7)	108.7(4)
C5	C4	C2		113.4(4)
C5	C4	C3		109.6(4)
C1	C4	C2		107.4(3)
C1	C4	C3		109.8(4)

Table 26 continued.

C2	C4	C3		107.9(4)
C6	C5	C10	1.388(9)	117.4(5)
C6	C5	C4		122.5(4)
C10	C5	C4	1.372(7)	120.1(5)
C7	C6	C5	1.376(12)	120.6(6)
C8	C7	C6	1.346(12)	121.5(9)
C9	C8	C7	1.391(14)	118.9(9)
C10	C9	C8	1.372(10)	119.6(6)
C5	C10	C9		121.9(6)
C12	C11	C16	1.415(6)	120.9(4)
C12	C11	N1		119.3(4)
C16	C11	N1	1.404(7)	119.7(4)
C13	C12	C17	1.392(6)	122.4(4)
C13	C12	C11		117.6(5)
C17	C12	C11	1.506(8)	120.1(4)
C14	C13	C12	1.369(9)	121.8(5)
C15	C14	C13	1.367(8)	120.2(5)
C16	C15	C14	1.394(6)	121.4(6)
C20	C16	C11	1.516(7)	121.0(4)
C20	C16	C15		120.7(5)
C11	C16	C15		118.2(5)
C18	C17	C19	1.523(7)	109.8(5)
C18	C17	C12		111.0(5)
C19	C17	C12	1.527(8)	114.7(4)
C21	C20	C22	1.532(7)	110.2(5)
C21	C20	C16		111.0(4)
C22	C20	C16	1.530(9)	114.8(4)
C24	C23	N2	1.374(9)	111.2(4)
C25	C24	C23	1.367(7)	104.9(5)
N3	C25	C24		108.7(5)
C27	C26	N4	1.372(8)	110.9(5)
C28	C27	C26	1.364(9)	105.0(5)
N5	C28	C27		108.7(5)
C30	C29	N6	1.383(8)	111.2(5)
C31	C30	C29	1.359(9)	104.5(5)
N7	C31	C30		109.3(5)

Table A.27: Anisotropic thermal parameters^a for the non-H atoms of compound 5.

Atom	U11	U22	U33	U12	U13	U23
Mo	0.0266(2)	0.0306(2)	0.0302(2)	-0.00813(14)	0.00034(14)	-0.00485(14)
O1	0.031(2)	0.049(2)	0.048(2)	-0.0133(15)	-0.0014(14)	-0.005(2)
N1	0.033(2)	0.035(2)	0.027(2)	-0.009(2)	0.001(2)	-0.006(2)
N2	0.027(2)	0.037(2)	0.035(2)	-0.010(2)	0.002(2)	-0.004(2)
N3	0.039(2)	0.041(2)	0.047(2)	-0.019(2)	0.006(2)	-0.015(2)
N4	0.034(2)	0.038(2)	0.044(2)	-0.009(2)	0.001(2)	-0.002(2)
N5	0.036(2)	0.032(2)	0.051(2)	-0.008(2)	0.007(2)	-0.006(2)
N6	0.040(2)	0.043(2)	0.033(2)	-0.013(2)	0.004(2)	-0.006(2)
N7	0.039(2)	0.043(2)	0.036(2)	-0.011(2)	0.005(2)	-0.012(2)
B	0.039(3)	0.036(3)	0.057(4)	-0.011(2)	0.006(3)	-0.017(3)
C1	0.039(3)	0.034(2)	0.031(2)	-0.013(2)	-0.003(2)	-0.001(2)
C2	0.075(4)	0.066(4)	0.042(3)	-0.018(3)	-0.010(3)	0.005(3)
C3	0.070(4)	0.064(3)	0.040(3)	-0.031(3)	0.008(3)	-0.016(3)
C4	0.054(3)	0.047(3)	0.030(2)	-0.019(2)	-0.001(2)	-0.005(2)
C5	0.056(3)	0.047(3)	0.030(2)	-0.021(2)	0.012(2)	-0.012(2)
C6	0.078(5)	0.058(4)	0.059(4)	-0.034(4)	0.018(3)	-0.015(3)
C7	0.095(6)	0.087(5)	0.089(5)	-0.059(5)	0.038(5)	-0.030(4)
C8	0.065(5)	0.134(8)	0.089(6)	-0.053(6)	0.034(5)	-0.061(6)
C9	0.058(4)	0.093(5)	0.064(4)	-0.004(4)	0.001(4)	-0.020(4)
C10	0.056(4)	0.062(4)	0.042(3)	-0.018(3)	0.008(3)	-0.009(3)
C11	0.036(2)	0.034(2)	0.024(2)	-0.012(2)	0.004(2)	-0.000(2)
C12	0.035(3)	0.037(2)	0.036(2)	-0.009(2)	0.007(2)	0.002(2)
C13	0.036(3)	0.050(3)	0.050(3)	0.000(2)	0.005(2)	0.002(2)
C14	0.061(4)	0.040(3)	0.057(3)	0.000(3)	0.013(3)	-0.009(3)
C15	0.065(4)	0.041(3)	0.046(3)	-0.020(3)	0.005(3)	-0.012(2)
C16	0.044(3)	0.034(2)	0.033(2)	-0.014(2)	0.008(2)	-0.002(2)
C17	0.034(3)	0.052(3)	0.051(3)	-0.012(2)	-0.006(2)	0.005(3)
C18	0.070(4)	0.090(4)	0.055(3)	-0.032(3)	-0.012(3)	-0.007(3)
C19	0.050(4)	0.107(5)	0.094(5)	-0.036(4)	-0.003(3)	-0.008(4)
C20	0.052(3)	0.040(3)	0.050(3)	-0.024(3)	-0.007(2)	0.002(2)
C21	0.050(3)	0.075(4)	0.064(4)	-0.029(3)	0.002(3)	-0.002(3)
C22	0.084(4)	0.074(4)	0.071(4)	-0.050(4)	-0.016(3)	-0.006(3)
C23	0.039(3)	0.042(3)	0.041(3)	-0.013(2)	0.002(2)	-0.007(2)
C24	0.031(3)	0.063(3)	0.061(3)	-0.022(3)	0.001(2)	-0.002(3)
C25	0.046(3)	0.053(3)	0.058(3)	-0.027(3)	-0.000(3)	-0.008(3)
C26	0.038(3)	0.056(3)	0.047(3)	-0.013(3)	-0.005(2)	0.000(3)
C27	0.039(3)	0.042(3)	0.080(4)	0.002(3)	0.002(3)	0.015(3)
C28	0.042(3)	0.035(3)	0.070(4)	-0.004(2)	0.006(3)	-0.000(3)
C29	0.042(3)	0.047(3)	0.047(3)	-0.013(2)	0.003(2)	0.003(2)
C30	0.045(3)	0.072(4)	0.032(3)	-0.011(3)	0.003(2)	-0.001(3)
C31	0.048(3)	0.067(4)	0.039(3)	-0.010(3)	-0.000(2)	-0.021(3)
C32	0.038(3)	0.073(4)	0.077(4)	-0.019(3)	-0.011(3)	-0.006(3)

^a U_{ij} are the mean-square amplitudes of vibration in Å² from the general temperature

factor expression $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^{*}b^{*}U_{12} + 2hla^{*}c^{*}U_{13} + 2klb^{*}c^{*}U_{23})]$

Table A.28: Fractional coordinates and isotropic thermal parameters ($\text{\AA}^2$) for the H atoms of compound 5.

Atom	x	y	z	U
H1	0.145(4)	0.285(4)	0.123(3)	0.024(12)
H	0.270(4)	-0.189(4)	0.094(3)	0.037(11)
H2a	0.21037	0.13694	0.59192	0.08
H2b	0.33183	0.11133	0.51689	0.08
H2c	0.22853	0.04392	0.5115	0.08
H3a	0.125030	0.40415	0.4442	0.08
H3b	0.27094	0.32814	0.47412	0.08
H3c	0.15103	0.35653	0.55062	0.08
H6	0.017(6)	0.107(5)	0.562(4)	0.08(2)
H7	-0.210(6)	0.130(5)	0.572(4)	0.08(2)
H8	-0.345(7)	0.281(6)	0.481(5)	0.10(3)
H9	-0.277(5)	0.416(5)	0.391(4)	0.06(2)
H10	-0.057(5)	0.382(4)	0.382(3)	0.042(14)
H13	-0.239(5)	0.595(4)	0.164(3)	0.045(13)
H14	-0.163(5)	0.733(5)	0.241(4)	0.07(2)
H15	0.062(5)	0.661(4)	0.289(3)	0.06(2)
H17	-0.079(5)	0.293(4)	0.139(3)	0.043(13)
H18a	-0.1312	0.44694	-0.016180	0.08
H18b	-0.11408	0.30924	-0.01754	0.08
H18c	0.00916	0.34778	0.00162	0.08
H19a	-0.32279	0.47079	0.11071	0.08
H19b	-0.29334	0.385	0.20254	0.08
H19c	-0.29523	0.33183	0.10237	0.08
H20	0.288(4)	0.384(4)	0.280(3)	0.021(10)
H21a	0.32077	0.53429	0.13167	0.08
H21b	0.32785	0.40046	0.11972	0.08
H21c	0.43856	0.42637	0.17507	0.08
H22a	0.26958	0.62104	0.30187	0.08
H22b	0.39009	0.508540	0.33628	0.08
H22c	0.24729	0.53647	0.38673	0.08
H23	-0.049(4)	0.143(4)	0.295(3)	0.028(12)
H24	-0.172(5)	0.016(4)	0.238(3)	0.049(14)
H25	0.012(4)	-0.136(4)	0.137(3)	0.044(13)
H26	0.479(4)	-0.076(3)	0.370(3)	0.019(11)
H27	0.586(5)	-0.288(4)	0.341(3)	0.06(2)
H28	0.460(5)	-0.311(5)	0.190(4)	0.06(2)
H29	0.352(5)	0.214(4)	-0.002(3)	0.052(14)
H30	0.385(5)	0.084(4)	-0.140(4)	0.055(15)
H31	0.335(5)	-0.105(5)	-0.077(4)	0.06(2)
H32a	0.59152	0.09539	0.30956	0.08
H32b	0.46416	0.18297	0.36357	0.08
H32c	0.54368	0.23509	0.28547	0.08

Table A.29: Bond Lengths (Å) and Angles (°) of the H atoms of compound 5.

1	2	3	1-2	1-2-3
H1	N1	C11	0.76(4)	109.(3)
H1	N1	Mo		109.(3)
H	B	N3	1.06(4)	113.(2)
H	B	N5		107.(2)
H	B	N7		111.(2)
H2a	C2	H2b	0.960(5)	109.5(6)
H2a	C2	H2c		109.5(6)
H2a	C2	C4		109.4(4)
H2b	C2	H2c	0.960(6)	109.5(5)
H2b	C2	C4		109.4(5)
H2c	C2	C4	0.960(6)	109.7(5)
H3a	C3	H3b	0.960(5)	109.5(6)
H3a	C3	H3c		109.5(4)
H3a	C3	C4		109.3(5)
H3b	C3	H3c	0.960(6)	109.5(6)
H3b	C3	C4		109.6(4)
H3c	C3	C4	0.960(5)	109.5(5)
H6	C6	C7	0.92(5)	126.(4)
H6	C6	C5		113.(4)
H7	C7	C8	0.93(6)	122.(4)
H7	C7	C6		116.(3)
H8	C8	C9	0.78(8)	119.(5)
H8	C8	C7		121.(5)
H9	C9	C10	0.91(5)	119.(4)
H9	C9	C8		121.(4)
H10	C10	C5	0.88(5)	120.(3)
H10	C10	C9		118.(3)
H13	C13	C14	0.93(5)	123.(3)
H13	C13	C12		115.(3)
H14	C14	C15	0.97(5)	120.(4)
H14	C14	C13		120.(4)
H15	C15	C16	0.95(6)	115.(3)
H15	C15	C14		124.(3)
H17	C17	C18	0.88(4)	104.(3)
H17	C17	C19		108.(3)
H17	C17	C12		109.(3)
H18a	C18	H18b	0.960(6)	109.5(6)
H18a	C18	H18c		109.5(7)
H18a	C18	C17		109.3(5)
H18b	C18	H18c	0.960(7)	109.5(5)
H18b	C18	C17		109.3(6)
H18c	C18	C17	0.960(6)	109.8(5)
H19a	C19	H19b	0.960(6)	109.5(6)
H19a	C19	H19c		109.5(6)
H19a	C19	C17		109.7(6)
H19b	C19	H19c	0.960(6)	109.5(7)

Table 29 continued.

H19b	C19	C17		109.4(5)
H19c	C19	C17	0.960(8)	109.3(5)
H20	C20	C21	0.89(4)	106.(2)
H20	C20	C22		108.(3)
H20	C20	C16		107.(3)
H21a	C21	H21b	0.960(6)	109.5(5)
H21a	C21	H21c		109.5(6)
H21a	C21	C20		109.6(4)
H21b	C21	H21c	0.960(6)	109.5(5)
H21b	C21	C20		109.4(6)
H21c	C21	C20	0.960(5)	109.3(5)
H22a	C22	H22b	0.960(6)	109.5(7)
H22a	C22	H22c		109.5(5)
H22a	C22	C20		109.7(5)
H22b	C22	H22c	0.960(6)	109.5(6)
H22b	C22	C20		109.5(5)
H22c	C22	C20	0.960(6)	109.1(6)
H23	C23	C24	0.80(4)	134.(3)
H23	C23	N2		115.(3)
H24	C24	C25	0.91(5)	127.(3)
H24	C24	C23		128.(3)
H25	C25	N3	0.95(5)	119.(3)
H25	C25	C24		132.(3)
H26	C26	C27	0.80(4)	128.(2)
H26	C26	N4		121.(2)
H27	C27	C28	0.91(4)	129.(3)
H27	C27	C26		126.(3)
H28	C28	N5	0.95(6)	114.(3)
H28	C28	C27		138.(3)
H29	C29	C30	0.96(6)	126.(3)
H29	C29	N6		123.(3)
H30	C30	C31	0.91(5)	131.(3)
H30	C30	C29		125.(3)
H31	C31	N7	0.96(6)	121.(3)
H31	C31	C30		130.(3)
H32a	C32	H32b	0.960(5)	109.5(5)
H32a	C32	H32c		109.5(5)
H32a	C32	O1		109.6(5)
H32b	C32	H32c	0.960(5)	109.5(6)
H32b	C32	O1		109.6(5)
H32c	C32	O1	0.960(7)	109.2(5)

Crystallographic Data for $[(\text{Me}_3\text{SiN})\text{C}_6\text{H}_4(\text{N}'\text{SiMe}_2\text{CH}_2)]\text{IW}(\text{NPh})(\text{CH}_2\text{C}(\text{CH}_3)_3)$, 16

Table A.30: Crystallographic Data

A. Crystal data (298 K)	16
a , Å	10.934(3)
b , Å	15.012(3)
c , Å	16.563(6)
α , deg.	90.00(0)
β , deg.	92.67(2)
γ , deg.	90.00(0)
V , Å ³	2715.7(9)
d_{calc} , g cm ⁻³ (298 K)	1.457
Empirical formula	C ₂₃ H ₃₇ N ₃ Si ₂ W
Formula wt, g	595.59
Crystal system	Monoclinic
Space group	P 2 ₁ /n
Z	4
$F(000)$, electrons	1192
Crystal size (mm ³)	0.31 x 0.24 x 0.22
B. Data collection (298 K)	
Radiation, λ (Å)	Mo-K α , 0.71073
Mode	ω -scan
Scan range	Symmetrically over 1.2° about K $\alpha_{1,2}$ maximum
Background	offset 1.0 and -1.0 in ω from K $\alpha_{1,2}$ maximum
Scan rate, deg. min. ⁻¹	15 – 30
2 θ range, deg.	3 – 45
Range of $h\ k\ l$	$\begin{array}{ccccccc} 0 & \leq & h & \leq & 11 \\ 0 & \leq & k & \leq & 16 \\ -17 & \leq & l & \leq & 17 \end{array}$
Total reflections measured	3931
Unique reflections	3539
Absorption coeff. μ (Mo-K α), mm ⁻¹	5.36
C. Structure refinement	
S , Goodness-of-fit	1.32
Reflections used, $I > 2\sigma(I)$	2234
No. of variables	262
R , wR^* (%)	5.28, 5.33
R_{int} (%)	5.04
Max. shift/esd	0.0003

Table A.30 continued.

min. peak in diff. four. map ($\text{e } \text{\AA}^{-3}$)	-0.90
max. peak in diff. four. map ($\text{e } \text{\AA}^{-3}$)	1.33

* Relevant expressions are as follows, where in the footnote F_o and F_c represent, respectively, the observed and calculated structure-factor amplitudes.

Function minimized was $w(|F_o| - |F_c|)^2$, where $w = (\sigma(F))^{-2}$

$$R = \sum(|F_o| - |F_c|) / \sum |F_o|$$

$$wR = [\sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}$$

$$S = [\sum w(|F_o| - |F_c|)^2 / (m-n)]^{1/2}$$

Table A.31: Fractional coordinates and equivalent isotropic^a thermal parameters ($\text{\AA}^2$) for the non-H atoms of compound **16**.

Atom	x	y	z	U
W	0.15343(6)	0.13675(5)	0.44004(4)	0.0408(2)
Si1	0.1508(5)	0.0364(3)	0.2856(3)	0.052(2)
Si2	0.3473(5)	0.2827(3)	0.5271(3)	0.051(2)
N1	0.1943(10)	0.0913(9)	0.5310(8)	0.044(5)
N2	0.1942(11)	0.1411(9)	0.3229(7)	0.044(4)
N3	0.2929(11)	0.2268(8)	0.4388(7)	0.042(5)
C1	0.2617(15)	0.0349(11)	0.5889(12)	0.048(7)
C2	0.234(2)	0.0318(12)	0.6689(10)	0.054(7)
C3	0.305(2)	-0.0204(14)	0.7219(11)	0.078(9)
C4	0.404(2)	-0.0699(13)	0.6958(13)	0.079(9)
C5	0.422(2)	-0.0691(14)	0.6171(14)	0.086(10)
C6	0.355(2)	-0.0186(13)	0.5636(12)	0.069(8)
C7	0.2868(15)	0.1977(11)	0.2995(9)	0.045(6)
C8	0.324(2)	0.2107(12)	0.2213(10)	0.062(8)
C9	0.429(2)	0.2657(13)	0.2114(13)	0.078(10)
C10	0.487(2)	0.3035(13)	0.2753(13)	0.073(9)
C11	0.448(2)	0.2932(11)	0.3506(10)	0.055(7)
C12	0.3443(14)	0.2433(10)	0.3649(9)	0.042(6)
C13	-0.0132(14)	0.2043(12)	0.4580(10)	0.058(7)
C14	-0.070(2)	0.2790(14)	0.4102(12)	0.063(8)
C15	0.015(2)	0.356(2)	0.414(2)	0.16(2)
C16	-0.187(2)	0.307(2)	0.442(2)	0.15(2)
C17	-0.084(2)	0.256(2)	0.3237(14)	0.17(2)
C18	0.099(2)	0.0101(11)	0.3844(9)	0.062(7)
C19	0.283(2)	-0.0327(11)	0.2542(12)	0.084(9)
C20	0.034(2)	0.0452(11)	0.2028(9)	0.066(8)
C21	0.4964(15)	0.2333(12)	0.5622(11)	0.074(8)
C22	0.359(2)	0.4047(11)	0.5056(11)	0.083(9)
C23	0.242(2)	0.2769(11)	0.6093(10)	0.068(8)

^aFor anisotropic atoms, the U value is U_{eq} , calculated as $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* A_{ij}$ where A_{ij} is the dot product of the i^{th} and j^{th} direct space unit cell vectors.

Table A.32: Bond Lengths (Å) and Angles (°) for the non-H atoms of compound **16**.

<u>1</u>	<u>2</u>	<u>3</u>	<u>1-2</u>	<u>1-2-3</u>
N1	W	N2	1.695(13)	144.0(5)
N1	W	N3		96.3(5)
N1	W	C13		105.1(6)
N2	W	N3	2.012(11)	76.7(5)
N2	W	C13		110.5(6)
N2	W	C18		71.9(6)
N3	W	C13	2.039(12)	109.4(6)
N3	W	C18		139.6(6)
C13	W	C18	2.12(2)	105.0(6)
C18	W	N1	2.18(2)	94.6(6)
N2	Si1	C18	1.747(14)	88.1(7)
N2	Si1	C19		113.2(7)
C18	Si1	C19	1.80(2)	114.2(8)
C18	Si1	C20		117.5(8)
C19	Si1	C20	1.88(2)	110.6(8)
C20	Si1	N2	1.83(2)	111.6(7)
N3	Si2	C21	1.766(12)	109.0(7)
N3	Si2	C22		109.3(7)
C21	Si2	C22	1.86(2)	112.6(8)
C21	Si2	C23		108.7(8)
C22	Si2	C23	1.87(2)	103.9(8)
C23	Si2	N3	1.82(2)	113.4(7)
C1	N1	W	1.45(2)	157.7(11)
C7	N2	W	1.39(2)	119.1(9)
C7	N2	Si1		129.8(10)
W	N2	Si1		104.1(6)
C12	N3	W	1.39(2)	117.3(9)
C12	N3	Si2		120.7(10)
W	N3	Si2		122.0(6)
C2	C1	C6	1.37(3)	118.(2)
C2	C1	N1		121.9(15)
C6	C1	N1	1.38(3)	120.(2)
C3	C2	C1	1.38(3)	119.(2)
C4	C3	C2	1.40(3)	121.(2)
C5	C4	C3	1.33(3)	117.(2)
C6	C5	C4	1.35(3)	123.(2)
C1	C6	C5		121.(2)
C8	C7	C12	1.39(2)	121.(2)
C8	C7	N2		126.4(14)
C12	C7	N2	1.40(2)	112.9(13)
C9	C8	C7	1.43(3)	117.(2)
C10	C9	C8	1.34(3)	121.(2)
C11	C10	C9	1.35(3)	122.(2)
C12	C11	C10	1.39(2)	121.(2)
N3	C12	C7		114.0(13)
N3	C12	C11		127.6(14)
C7	C12	C11		118.2(14)

Table 32 continued.

C14	C13	W	1.49(3)	128.8(12)
C15	C14	C16	1.48(3)	108.(2)
C15	C14	C17		105.(2)
C15	C14	C13		108.(2)
C16	C14	C17	1.46(3)	111.(2)
C16	C14	C13		112.(2)
C17	C14	C13	1.47(3)	111.(2)
W	C18	Si1		95.9(7)

Table A.33: Anisotropic thermal parameters^a for the non-H atoms of compound 16.

Atom	U11	U22	U33	U12	U13	U23
W	0.0366(4)	0.0484(4)	0.0379(3)	-0.0066(5)	0.0076(2)	0.0060(5)
Si1	0.051(3)	0.052(3)	0.052(3)	-0.001(3)	-0.001(3)	-0.009(3)
Si2	0.056(3)	0.048(3)	0.050(3)	-0.009(3)	0.003(3)	-0.002(2)
N1	0.011(7)	0.060(9)	0.062(9)	-0.005(7)	0.008(6)	-0.038(8)
N2	0.049(8)	0.034(7)	0.047(7)	0.004(9)	-0.005(6)	0.004(8)
N3	0.040(8)	0.051(9)	0.034(7)	-0.010(7)	-0.001(6)	0.004(7)
C1	0.023(10)	0.033(11)	0.091(15)	-0.014(9)	0.030(10)	-0.017(10)
C2	0.046(11)	0.068(13)	0.047(11)	0.001(10)	0.006(9)	0.019(10)
C3	0.09(2)	0.08(2)	0.062(13)	-0.018(14)	-0.004(12)	0.033(12)
C4	0.08(2)	0.063(15)	0.09(2)	0.034(13)	-0.018(13)	0.015(13)
C5	0.09(2)	0.08(2)	0.09(2)	0.018(14)	0.025(14)	0.016(15)
C6	0.064(13)	0.074(14)	0.070(12)	-0.018(14)	0.018(11)	0.021(14)
C7	0.049(11)	0.048(12)	0.039(10)	0.002(10)	0.015(9)	0.012(9)
C8	0.077(15)	0.060(14)	0.051(12)	0.020(12)	0.021(11)	0.010(10)
C9	0.11(2)	0.06(2)	0.07(2)	0.022(14)	0.055(15)	0.031(13)
C10	0.09(2)	0.060(15)	0.07(2)	-0.007(13)	0.025(14)	0.024(13)
C11	0.059(12)	0.050(12)	0.057(12)	-0.024(10)	0.016(10)	-0.006(9)
C12	0.043(10)	0.041(10)	0.045(10)	-0.002(9)	0.021(9)	0.001(9)
C13	0.037(10)	0.071(14)	0.067(12)	0.015(10)	0.008(9)	0.027(11)
C14	0.037(12)	0.08(2)	0.071(14)	-0.011(12)	0.009(10)	0.002(12)
C15	0.10(2)	0.12(2)	0.25(4)	0.06(2)	-0.02(2)	0.05(3)
C16	0.06(2)	0.20(3)	0.19(3)	0.07(2)	0.04(2)	0.05(2)
C17	0.22(3)	0.18(3)	0.11(2)	0.12(3)	-0.08(2)	-0.01(2)
C18	0.063(13)	0.059(13)	0.064(12)	-0.026(11)	-0.010(10)	-0.008(10)
C19	0.072(14)	0.060(13)	0.12(2)	-0.018(12)	0.022(13)	-0.029(13)
C20	0.11(2)	0.041(12)	0.048(11)	-0.010(11)	0.003(11)	-0.002(9)
C21	0.068(14)	0.067(14)	0.087(14)	0.007(12)	-0.014(11)	-0.006(12)
C22	0.10(2)	0.053(13)	0.090(15)	-0.006(12)	-0.009(13)	-0.011(12)
C23	0.076(15)	0.053(13)	0.075(13)	0.010(11)	0.001(11)	-0.018(11)

^a U_{ij} are the mean-square amplitudes of vibration in Å² from the general temperature

factor expression $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^{*}b^{*}U_{12} + 2hla^{*}c^{*}U_{13} + 2klb^{*}c^{*}U_{23})]$

Table A.34: Fractional coordinates and isotropic thermal parameters ($\text{\AA}^2$) for the H atoms of compound **16**.

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>	<u>U</u>
H2	0.1667	0.06532	0.68796	0.08
H3	0.28685	-0.02089	0.77805	0.08
H4	0.45203	-0.10596	0.73291	0.08
H5	0.48872	-0.10355	0.59811	0.08
H6	0.37488	-0.02051	0.50772	0.08
H8	0.28167	0.18267	0.17594	0.08
H9	0.45426	0.27828	0.15792	0.08
H10	0.56039	0.33678	0.26682	0.08
H11	0.49231	0.3221	0.39484	0.08
H13a	-0.005	0.22568	0.51256	0.08
H13b	-0.07458	0.15853	0.4543	0.08
H15a	0.02739	0.37559	0.46932	0.08
H15b	-0.02116	0.40335	0.38238	0.08
H15c	0.09169	0.33934	0.39332	0.08
H16a	-0.17663	0.32529	0.49723	0.08
H16b	-0.24025	0.256840	0.4374	0.08
H16c	-0.22127	0.35572	0.41024	0.08
H17a	-0.13804	0.20529	0.31969	0.08
H17b	-0.0063	0.24017	0.30346	0.08
H17c	-0.11915	0.30418	0.29253	0.08
H18a	0.01313	-0.00148	0.38559	0.08
H18b	0.14399	-0.03893	0.40857	0.08
H19a	0.254360	-0.08904	0.2338	0.08
H19b	0.33838	-0.04219	0.3003	0.08
H19c	0.32587	-0.00216	0.21289	0.08
H20a	0.01276	-0.01323	0.18327	0.08
H20b	0.0656	0.07972	0.15948	0.08
H20c	-0.03664	0.07387	0.22255	0.08
H21a	0.5273	0.26331	0.61009	0.08
H21b	0.55314	0.2403	0.52015	0.08
H21c	0.4864	0.17106	0.57362	0.08
H22a	0.41365	0.4127	0.46257	0.08
H22b	0.39086	0.43482	0.55314	0.08
H22c	0.28006	0.42889	0.4898	0.08
H23a	0.22987	0.21584	0.62407	0.08
H23b	0.16564	0.30307	0.59189	0.08
H23c	0.27644	0.30901	0.65522	0.08

Table A.35: Bond Lengths (Å) and Angles (°) of the H atoms of compound 16.

1	2	3	1-2	1-2-3
H2	C2	C3	0.96(2)	120.(2)
H2	C2	C1		120.(2)
H3	C3	C4	0.96(2)	119.(2)
H3	C3	C2		119.(2)
H4	C4	C5	0.96(2)	122.(2)
H4	C4	C3		121.(2)
H5	C5	C6	0.96(2)	119.(2)
H5	C5	C4		118.(2)
H6	C6	C1	0.96(2)	121.(2)
H6	C6	C5		118.(2)
H8	C8	C9	0.96(2)	121.(2)
H8	C8	C7		121.(2)
H9	C9	C10	0.96(2)	120.(2)
H9	C9	C8		119.(2)
H10	C10	C11	0.96(2)	120.(2)
H10	C10	C9		118.(2)
H11	C11	C12	0.96(2)	120.(2)
H11	C11	C10		119.(2)
H13a	C13	H13b	0.96(2)	109.(2)
H13a	C13	C14		105.(2)
H13a	C13	W		104.4(11)
H13b	C13	C14	0.96(2)	103.3(14)
H13b	C13	W		104.6(12)
H15a	C15	H15b	0.96(3)	109.(2)
H15a	C15	H15c		109.(2)
H15a	C15	C14		110.(2)
H15b	C15	H15c	0.96(2)	109.(3)
H15b	C15	C14		108.(2)
H15c	C15	C14	0.96(2)	110.(2)
H16a	C16	H16b	0.96(3)	109.(2)
H16a	C16	H16c		109.(3)
H16a	C16	C14		111.(2)
H16b	C16	H16c	0.96(2)	109.(2)
H16b	C16	C14		106.(2)
H16c	C16	C14	0.96(2)	111.(2)
H17a	C17	H17b	0.96(3)	109.(3)
H17a	C17	H17c		109.(2)
H17a	C17	C14		107.(2)
H17b	C17	H17c	0.96(3)	109.(2)
H17b	C17	C14		110.(2)
H17c	C17	C14	0.96(3)	111.(2)
H18a	C18	H18b	0.96(2)	109.(2)
H18a	C18	W		113.3(12)
H18a	C18	Si1		114.0(12)
H18b	C18	W	0.96(2)	111.7(12)
H18b	C18	Si1		111.9(13)

Table A.35 continued.

H19a	C19	H19b	0.96(2)	109.(2)
H19a	C19	H19c		109.(2)
H19a	C19	Si1		109.6(13)
H19b	C19	H19c	0.96(2)	109.(2)
H19b	C19	Si1		108.9(14)
H19c	C19	Si1	0.96(2)	109.8(13)
H20a	C20	H20b	0.96(2)	109.5(15)
H20a	C20	H20c		109.(2)
H20a	C20	Si1		109.8(12)
H20b	C20	H20c	0.96(2)	109.(2)
H20b	C20	Si1		109.9(14)
H20c	C20	Si1	0.96(2)	108.8(11)
H21a	C21	H21b	0.96(2)	109.(2)
H21a	C21	H21c		109.(2)
H21a	C21	Si2		109.9(13)
H21b	C21	H21c	0.96(2)	109.(2)
H21b	C21	Si2		108.4(13)
H21c	C21	Si2	0.96(2)	110.1(12)
H22a	C22	H22b	0.96(2)	109.(2)
H22a	C22	H22c		109.(2)
H22a	C22	Si2		108.3(13)
H22b	C22	H22c	0.96(2)	109.(2)
H22b	C22	Si2		109.3(14)
H22c	C22	Si2	0.96(2)	110.8(14)
H23a	C23	H23b	0.96(2)	109.(2)
H23a	C23	H23c		109.(2)
H23a	C23	Si2		109.8(13)
H23b	C23	H23c	0.96(2)	109.(2)
H23b	C23	Si2		109.1(13)
H23c	C23	Si2	0.96(2)	109.5(13)

APPENDIX B
TABLES OF KINETIC AND CIMS DATA

Table B.1. Tabulated Kinetic Data for the Thermolysis of 13 in the Absence of PMe3.

Temp.	Run #1		Run #2		Run #3		Run averages		Error Data	
	Np #1 10 ⁴ sec ⁻¹	TMS #1 10 ⁴ sec ⁻¹	Np #2 10 ⁴ sec ⁻¹	TMS #2 10 ⁴ sec ⁻¹	Np #3 10 ⁴ sec ⁻¹	TMS #3 10 ⁴ sec ⁻¹	Np ave. 10 ⁴ sec ⁻¹	TMS ave. 10 ⁴ sec ⁻¹	std dev, s	1.96 s _x
80 °C	0.681	0.681	0.600	0.600	0.638	0.663	0.640	0.648	0.041	0.046
90 °C	1.79	1.84	1.76	1.82	1.70	1.81	1.75	1.82	0.030	0.034
100 °C	5.47	5.44	4.61	4.69	4.72	4.70	4.93	4.94	0.447	0.540
110 °C	12.72	12.42	12.16	12.86	11.16	11.19	12.01	12.16	0.788	0.892

Enthalpy of Activation, ΔH [‡]	25.6 ± 0.3 kcal/mol
Entropy of Activation, ΔS [‡]	-5.4 ± 0.8 cal/molK

Temp.	Run #1		Run #2		Run #3		Run averages		Error Data	
	Np #1 10 ⁴ sec ⁻¹	TMS #1 10 ⁴ sec ⁻¹	Np #2 10 ⁴ sec ⁻¹	TMS #2 10 ⁴ sec ⁻¹	Np #3 10 ⁴ sec ⁻¹	TMS #3 10 ⁴ sec ⁻¹	Np ave. 10 ⁴ sec ⁻¹	TMS ave. 10 ⁴ sec ⁻¹	std dev, s	1.96 s _x
90 °C	0.408	0.447					0.408	0.447	na	na
100 °C	1.27	1.30	1.27	1.30	1.21	1.26	1.25	1.29	0.029	0.033

Kinetic Isotope Effect Measured at 90 °C: k_H/k_D = 4.2
Kinetic Isotope Effect Measured at 100 °C: k_H/k_D = 3.9 ± 0.4

Table B.2. Tabulated Kinetic Data for the Thermolysis of **13** in the Presence of PMe₃.

Temp.	Run #1		Run #2		Run #3		Run averages			Error Data	
	Np #1 10 ⁴ sec ⁻¹	TMS #1 10 ⁴ sec ⁻¹	Np #2 10 ⁴ sec ⁻¹	TMS #2 10 ⁴ sec ⁻¹	Np #3 10 ⁴ sec ⁻¹	TMS #3 10 ⁴ sec ⁻¹	Np ave. 10 ⁴ sec ⁻¹	TMS ave. 10 ⁴ sec ⁻¹	k, average	std dev, s	1.96 s _x
80 °C	0.539	0.517	0.369	0.383	0.462	0.465	0.457	0.455	0.456	0.076	0.086
90 °C	1.14	1.27	1.42	1.52		1.42	1.28	1.40	1.34	0.141	0.160
100 °C	3.80	4.44	3.74	4.04	4.66	3.96	4.07	4.15	4.11	0.209	0.236
110 °C	9.42	9.67	11.28	10.87	12.28	13.11	11.00	11.22	11.10	1.576	1.783

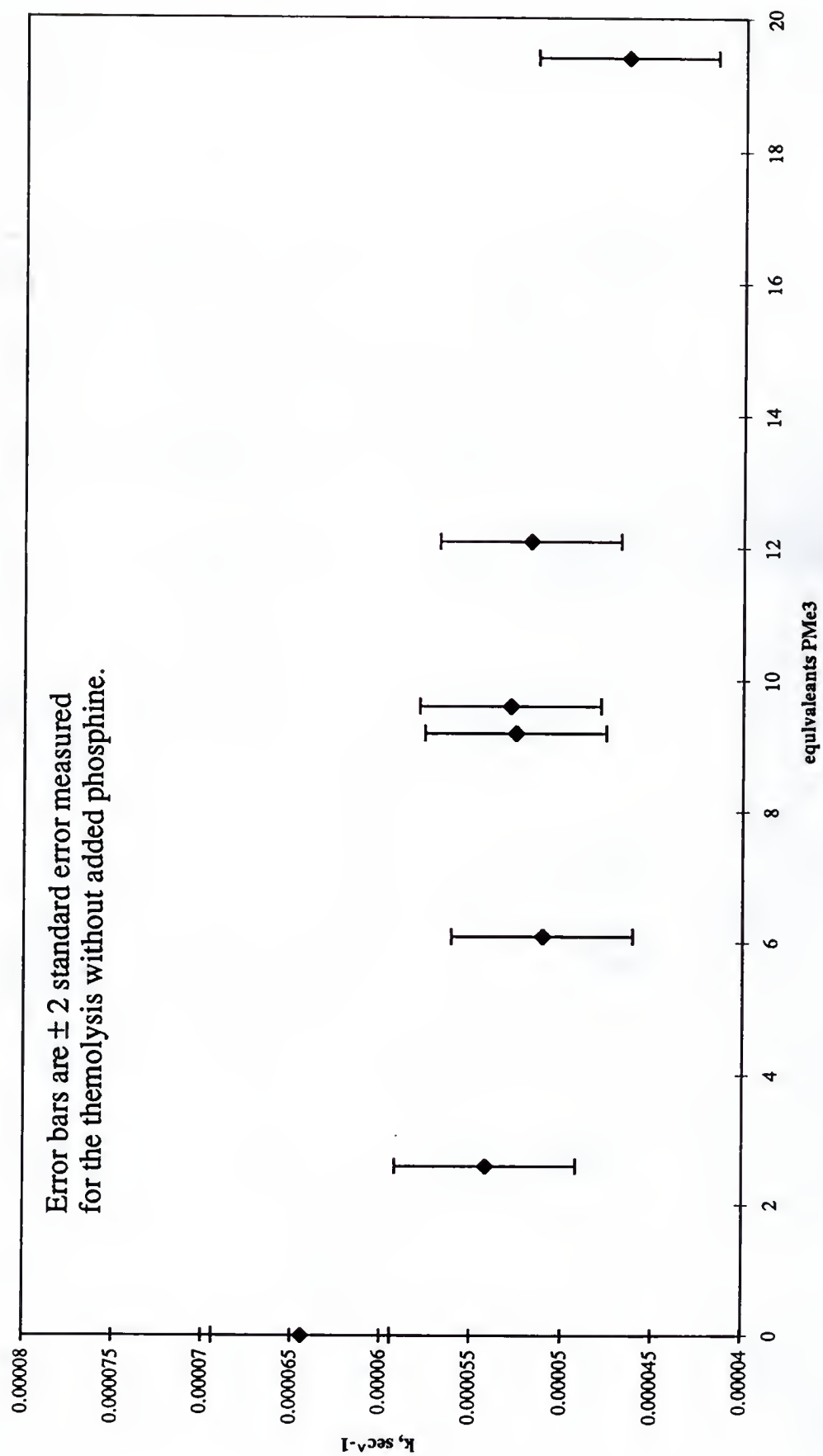
Enthalpy of Activation, ΔH [‡]	28.1 ± 0.3 kcal/mol
Entropy of Activation, ΔS [‡]	0.8 ± 0.8 cal/molK

Temp.	Run #1		Run #2		Run #3		Run averages			Error Data	
	Np #1 10 ⁴ sec ⁻¹	TMS #1 10 ⁴ sec ⁻¹	Np #2 10 ⁴ sec ⁻¹	TMS #2 10 ⁴ sec ⁻¹	Np #3 10 ⁴ sec ⁻¹	TMS #3 10 ⁴ sec ⁻¹	Np ave. 10 ⁴ sec ⁻¹	TMS ave. 10 ⁴ sec ⁻¹	k, average	std dev, s	1.96 s _x
100 °C	0.700	0.700	0.892	0.881			0.796	0.791	0.793	0.132	0.183

Kinetic Isotope Effect Measured at 100 °C: k_H/k_D = 5.2 ± 0.9

Table B.3. Observed m/z Values for CIMS Analyses of Thermolysis Reactions.

temp, solvent	PMe ₃ , equiv.	m/z 57	m/z 58	m/z 59	m/z 60	m/z 61
80 °C, C ₇ H ₈	0	49.6	7.1	55.6	100	3.9
80 °C, C ₆ D ₆	0	51.0	5.9	48.6	100	2.6
100 °C, C ₇ D ₈	5	36.9 (8.7)	4.4 (0.1)	18.9 (2.3)	100	3.2 (0.7)
	0	61.6	7.9	66.1	100	2.4
110 °C, C ₇ H ₈	20	31.7 (2.0)	2.3 (0.2)	9.2 (0.6)	100	2.3 (0.9)
	0	59.0	7.9	80.0	100	2.4
25 °C, C ₆ D ₆	H ₂	40.3	8.4	100	12.6	0.1

Table B.4. Rate of Thermolysis versus PMe₃ at 80 °C

LIST OF REFERENCES

1. Ivin, K. J. *Olefin Metathesis*; Academic Press: New York, 1982.
2. Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; G. Wilkinson and F. G. A. Stone, Eds.; Pergamon Press: Oxford, 1982; Vol. 8; pp 499.
3. Hérissou, J. L.; Chauvin, Y. *Makromol. Chem.* **1970**, *141*, 161.
4. Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.
5. Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; 2 ed.; University Science Books: Mill Valley, 1987.
6. Chatt, J.; Dilworth, J. R. *J. Indian Chem. Soc.* **1977**, *54*, 13.
7. Young, C. G.; Janos, F.; Bruck, M., A.; Wexler, P. A.; Enemark, J. H. *Aust. J. Chem.* **1990**, *43*, 1347.
8. Schrock, R. R. *Reactions of Coordinated Ligands*; Plenum: New York, 1986.
9. Griffith, W. P. *Coord. Chem. Rev.* **1970**, *5*, 459.
10. Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.
11. Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239.
12. Rappé, A. K.; Goddard, W. A., III *J. Am. Chem. Soc.* **1982**, *104*, 448.
13. Lin, Z.; Hall, M. B. *Coord. Chem. Rev.* **1993**, *123*, 149.
14. Cundari, T. R.; Gordon, M. S. *Organometallics* **1992**, *11*, 55.
15. Brower, D. C.; Templeton, J. L.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1987**, *109*, 5203.
16. Tatsumi, K.; Hoffmann, R. *Inorg. Chem.* **1980**, *19*, 2656.
17. Haymore, B. L.; Maatta, E. A.; Wentworth, R. A. D. *J. Am. Chem. Soc.* **1979**, *101*, 2063.
18. Maatta, E. A.; Wentworth, R. A. D. *Inorg. Chem.* **1979**, *18*, 2409.

19. *Transition Metal Carbene Chemistry*; Seyferth, D., Ed.; Verlag Chemie: Weinheim, 1983.
20. Fischer, E. O.; Maasböl, A. *Angew. Chem. , Int. Ed. Engl.* **1964**, *3*, 580.
21. Schrock, R. R.; Meakin, P. *J. Am. Chem. Soc.* **1974**, *96*, 5288.
22. Taylor, T. E.; Hall, M. B. *J. Am. Chem. Soc.* **1984**, *106*, 1576.
23. Carter, E.; Goddard III, W. A. *J. Am. Chem. Soc.* **1986**, *108*, 4746.
24. Fryzuk, M. D.; Mao, S. S. H.; Zaworotko, M. J.; MacGillivray, L. R. *J. Am. Chem. Soc.* **1993**, *115*, 5336.
25. Meinhart, J. D.; Anslyn, E. V.; Grubbs, R. H. *Organometallics* **1989**, *8*, 583.
26. Toreki, R.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 3367.
27. Gagné, M. R.; Grubbs, R. H.; Feldman, J.; Ziller, J. W. *Organometallics* **1992**, *11*, 3933.
28. LaPointe, A. M.; Schrock, R. R. *Organometallics* **1993**, *12*, 3379.
29. Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611.
30. Tulip, T. H.; Thorn, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 2448.
31. Andersen, R. A.; Jones, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 446.
32. Andreucci, L.; Diversi, P.; Ingrosso, G.; Lucherini, A.; Marchetti, F.; Adovasio, V.; Nardelli, M. *J. Chem. Soc., Dalton Trans.* **1986**, 477.
33. Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2214.
34. Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 11831.
35. Bloch, L. L. Ph.D. Dissertation, University of Florida, 1993.
36. Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 7588.
37. Schrock, R. R.; Crowe, W. E.; Bazaz, G. C.; DiMare, M.; O'Regan, M. B.; Schofield, M. H. *Organometallics* **1991**, *10*, 1832.
38. Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359.
39. Horton, A. D.; Schrock, R. R.; Freudenberger, J. H. *Organometallics* **1987**, *6*, 893.
40. Ehrenfeld, D.; Kress, J.; Moore, B. D.; Osborn, J. A.; Schoettel, G. *J. Chem. Soc., Chem. Commun.* **1987**, 129.

41. Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; C.; Betz, P. *Organometallics* **1990**, *9*, 2262.
42. Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.
43. Pederson, S. F.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 7483.
44. Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1985**, *4*, 1937.
45. Schaverien, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2771.
46. Schwartz, J.; Gell, K. I. *J. Organomet. Chem.* **1980**, *184*, C1.
47. Johnson, L. K.; Virgil, S. C.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 5384.
48. Johnson, L. K.; Frey, M.; Ulibarri, T. A.; Virgil, S. C.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 8167.
49. Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1.
50. Legzdins, P.; Veltheer, J. E.; Young, M. A.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1995**, *14*, 407.
51. Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 1502-.
52. Clawson, L.; Buchwald, S. L.; Grubbs, R. H. *Tetrahedron Lett.* **1984**, 5733.
53. Mango, F. D.; Schachtschneider, J. H. *J. Am. Chem. Soc.* **1967**, *89*, 2484.
54. Calderon, N.; Ofstead, E. A.; Ward, J. P.; Judy, W. A.; Scott, K. W. *J. Am. Chem. Soc.* **1968**, *90*, 4133.
55. Wagener, K. B.; Boncella, J. M.; Nel, J. G. *Macromolecules* **1991**, *24*, 2649.
56. Wagener, K. B. In *The Third Chemical Congress of North America*; American Chemical Society: Toronto, 1988; pp 101.
57. Lindmark-Hamberg, M.; Wagener, K. B. *Macromolecules* **1987**, *20*, 2249.
58. Wagener, K. B.; Boncella, J. M.; Nel, J. G.; Duttweiler, R. P.; Hillmyer, M. A. *Makromol.Chem.* **1990**, *191*, 365.
59. Wagener, K. B.; Ruts, R. D.; Smith, D. W. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 419.
60. Marmo, J. C.; Wagener, K. B. *Macromolecules* **1993**, *26*, 2137.
61. Schrock, R. R. *J.Organomet. Chem.* **1986**, *300*, 249.

62. Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Missert, J. R.; Youngs, W. *J. J. Am. Chem. Soc.* **1980**, *102*, 4515.
63. Wengrovius, J. H.; Schrock, R. R. *Organometallics* **1982**, *1*, 148.
64. Rocklage, S. M.; Fellmann, J. D.; Rupprecht, G. A.; Messerle, L. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 1440.
65. Feldman, J.; DePue, R. T.; Schaverien, C. J.; Davis, W. M.; Schrock, R. R. In *Advances in Metal Carbene Chemistry*; U. Schubert, Ed.; Kluwer Academic Publishers: Boston, 1989; pp 323.
66. Wagener, K. B.; Brzezinska, K. *Macromolecules* **1991**, *24*, 5273.
67. O'Gara, J. E.; Portmess, J. D.; Wagener, K. B. *Macromolecules* **1993**, *26*, 2837.
68. Patton, J. T.; Boncella, J. M.; Wagener, K. B. *Macromolecules* **1992**, *25*, 3862.
69. Wagener, K. B.; Patton, J. T. *Macromolecules* **1993**, *26*, 249.
70. Wagener, K. B.; Smith, D. W. *Macromolecules* **1991**, *24*, 6073.
71. Smith, D. W.; Wagener, K. B. *Macromolecules* **1993**, *26*, 1633.
72. McConville, D. H.; Wolf, J. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 4413.
73. Heppert, J. A.; Dietz, S. D.; Eilerts, N. W.; Henning, R. W.; Morton, M. D.; Tukasagawa, F.; Kaul, F. A. *Organometallics* **1993**, *12*, 2565.
74. Shih, K. Y.; Totland, K.; Seidel, S. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 12103.
75. van der Schaaf, P. A.; Abbenhuis, R. A. T. M.; van der Noort, W. P. A.; deGraf, R.; Grove, D. M.; Smeets, W. J. J.; Spek, A. J.; van Koten, G. *Organometallics* **1994**, *13*, 1433.
76. Bloch, L. L.; Abboud, K.; Boncella, J. M. *J. Am. Chem. Soc.* **1991**, *113*, 7066.
77. Bloch, L. L.; Gamble, A. S.; Abboud, K.; Boncella, J. M. *Organometallics* **1992**, *11*, 2342.
78. Gamble, A. S.; Boncella, J. M. *Organometallics* **1993**, *12*, 2814.
79. VanderLende, D. D.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1994**, *13*, 3378.
80. Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170.
81. Trofimenko, S. *Acc. Chem. Res.* **1971**, *4*, 17.
82. Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.
83. Bloch, L. L.; Gamble, A. S.; Boncella, J. M. *J. Mol. Cat.* **1992**, *76*, 229.

84. VanderLende, D. D. Ph.D. Dissertation, University of Florida, 1994.
85. Vaughan, W. M.; Abboud, K. A.; Boncella, J. M. *J. Organomet. Chem.* **1995**, *485*, 37.
86. Vaughan, W. M.; Boncella, J. M.; Abboud, K. A. *Acta. Crystallogr. C.* **1994**, in press.
87. Vaughan, W. M.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1995**, *14*, 1567.
88. Curtis, M. D.; Shiu, K. *Inorg. Chem.* **1985**, *24*, 1218.
89. Hinkle, R. J.; Stang, P. J.; Arif, A. M. *Organometallics* **1993**, *12*, 3510.
90. Lawrance, G. *Chem. Rev.* **1986**, *86*, 17.
91. Lincoln, S.; Koch, S. A. *Inorg. Chem.* **1986**, *25*, 1594.
92. Lai, R.; Piasco, P.; Belin, C.; Ros, C.; Feneau-Dupont, J.; Declercq, J. P. *Polyhedron* **1993**, *12*, 2513.
93. Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423.
94. Chien, J. C. W.; Tsai, W.-M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570.
95. Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623.
96. Silverstein, R. M.; Bassler, G. C. *Spectrometric Identification of Organic Compounds*; John Wiley & Sons: New York, 1981.
97. Brookhart, M.; Grabt, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920.
98. Wu, T. K.; Pruckmayr, G. *Macromolecules* **1975**, *8*, 77.
99. Schnabel, R. C.; Roddick, D. M. *Organometallics* **1993**, *1993*, 704.
100. Yamamoto, A. *Organotransition Metal Chemistry*; John Wiley & Sons: New York, 1986.
101. Kress, J.; Osborn, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 3953.
102. Kress, J.; Osborn, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6346.
103. Kress, J.; Aguero, A.; Osborn, J. A. *J. Mol. Catal.* **1986**, *36*, 1.
104. Kress, J.; Osborn, J. A.; Greene, R. M. E.; Ivin, K. J.; Rooney, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 899.
105. Schrock, R. R.; Luo, S.; Zanetti, N. C.; Fox, H. H. *Organometallics* **1994**, *13*, 3396.

106. Rothwell, I. P. *Polyhedron* **1985**, *4*, 177.
107. Smith, G. M.; Carpenter, J. D.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 6805.
108. Bruno, J. W.; G.M., S.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40.
109. Diversi, P.; Ingrosso, G.; Lucherini, A.; Fasce, D. *J. Chem. Soc., Chem. Commun.* **1982**, 945.
110. Simpson, S. J.; Andersen, D. A. *Inorg. Chem.* **1981**, *20*, 3627.
111. Simpson, S. J.; Turner, H. W.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 2991.
112. Chamberlain, L.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 7338.
113. Chamberlain, L. R.; Rothwell, A. P.; Rothwell, I. P. *J. Am. Chem. Soc.* **1984**, *106*, 1847.
114. Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982.
115. Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L. M.; Latesky, S. L.; McMullen, A. K.; Steffey, B. D.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6068.
116. Hofmann, P.; Frede, M.; Stauffert, P.; Lasser, W.; Thewalt, U. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 712.
117. Berg, F. J.; Petersen, J. L. *Organometallics* **1991**, *10*, 1599.
118. Caulton, K. G.; Chisholm, M. H.; Streib, W. E.; Xue, Z. *J. Am. Chem. Soc.* **1991**, *113*, 6082.
119. Legzdins, P.; Rettig, S. J.; Veltheer, J. E.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1993**, *12*, 3575.
120. Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210.
121. Sheldrick, G. M. *SHELXTL plus* software package. Nicolet XRD Corporation: Madison, Wisconsin, 1990.
122. Reidel, D. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV, pp 55.
123. Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.
124. Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.
125. Spatz, C.; Johnston, J. O. *Basic Statistics: Tales of Distribution*; 4 ed.; Brooks/Cole Publishing Company: Pacific Grove, CA, 1989.

126. Microsoft Excel 5.0 spreadsheet program. Microsoft Corporation: Seattle, 1994.

BIOGRAPHICAL SKETCH

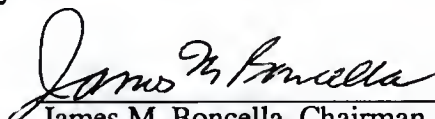
William Michael Vaughan began his career in chemistry at Hendrix College, Conway, Arkansas, in 1986. At Hendrix, he received the Award for First Year Chemistry, the Shideler Organic Chemistry Award, the ACS Award in Analytical Chemistry, and the McHenry Chemistry Award for outstanding senior major. In 1990, he graduated *summa cum laude* in chemistry with distinction. Enough of that; it never made a molecule.

Vaughan began research in chemistry working summers at Great Lakes Chemical Corporation, El Dorado, Arkansas. For three summers under Drs. Gary Lundquist and Stephen Brown, Vaughan was involved in applied research to support plant processes. Also during summers in college, he attended Army Reserve Officers' Training Corps camps at Ft. Knox, Kentucky, and Ft. Riley, Kansas, which culminated in his commission as a Second Lieutenant in the US Army in 1990.

Vaughan petitioned for an educational delay from active duty in order to attend the University of Florida for graduate studies in inorganic chemistry. He joined the research group of Dr. James M. Boncella and worked in the area of chelate-stabilized metal alkylidene complexes. Also while attending Florida, he won the 1992 Polymer Chemistry Diving Championship, teamed with Jim Boncella, Larry Villanueva, and Dan VanderLende to win the 1993 Analytical Open Golf Tournament, served as the Chemistry Department football seating bloc czar and inaugurated the notorious Annual Blue Springs Hog Roasts.

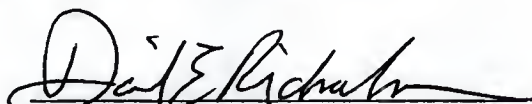
Upon graduation and marriage to Pamela Pippin, CPT Vaughan will serve his commission in the Army Medical Service Corps conducting research in the area of drug delivery systems at the Institute of Dental Research, Ft. Meade, Maryland.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



James M. Boncella, Chairman
Associate Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



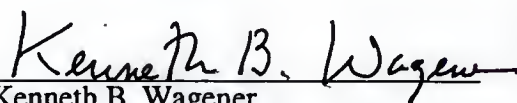
David E. Richardson
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



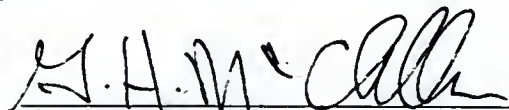
William M. Jones
Distinguished Service Professor of
Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Kenneth B. Wagener
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Guerry H. McClellan
Professor of Geology

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry of the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

May, 1995

Dean, Graduate School

LD
1780
1995
.V371

